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SUPPLEMENT TO MELLOR'S COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

VOLUME V

PART A: BORON–OXYGEN COMPOUNDS

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

By J. W. Mellor, D.Sc., F.R.S.

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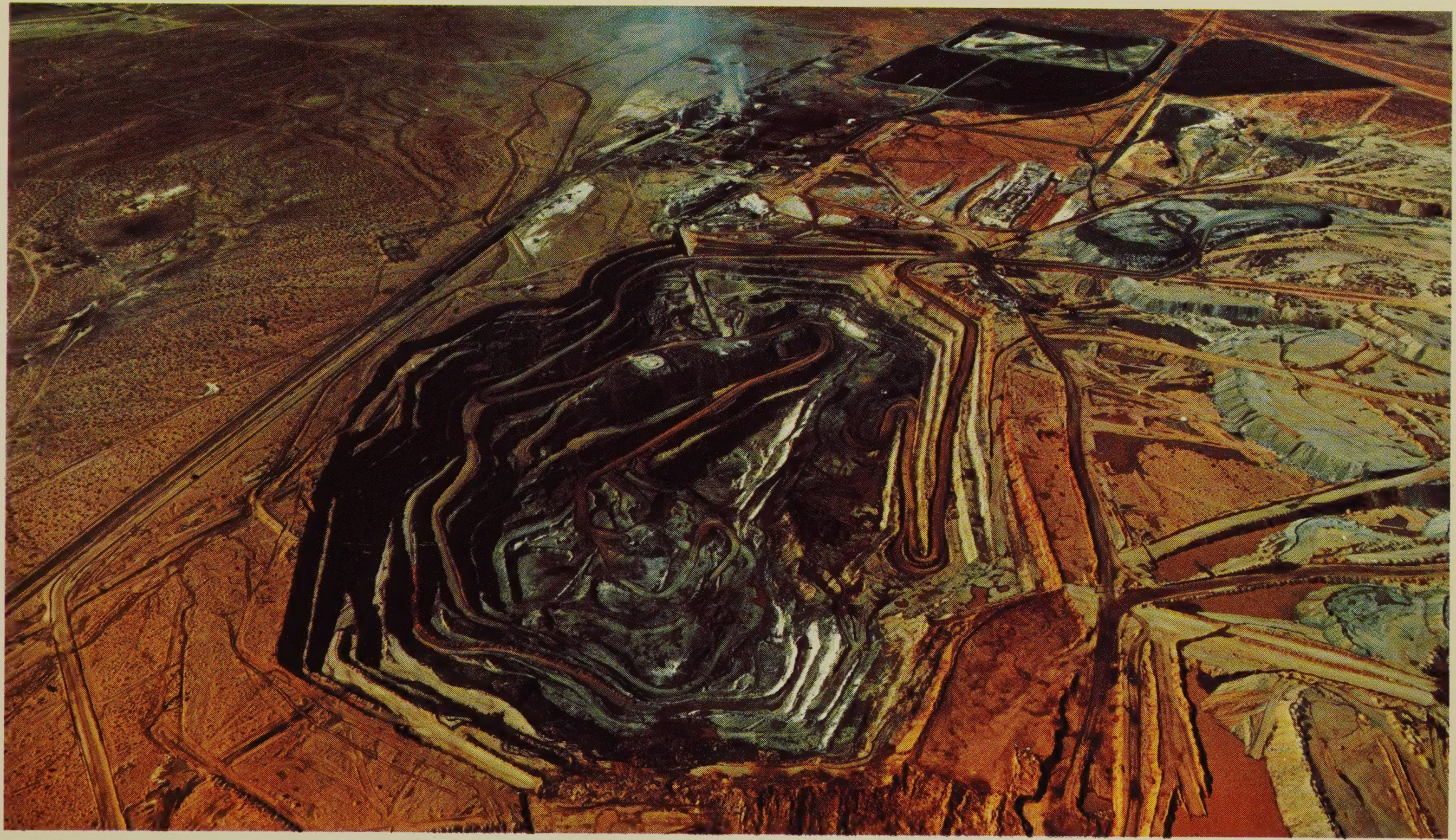

FRONTISPIECE.—U.S. Borax & Chemical Corporation opencast sodium borate mine and adjacent refinery at Boron, California

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pt. A

Supplement to

MELLOR'S COMPREHENSIVE
TREATISE ON

INORGANIC AND THEORETICAL CHEMISTRY

Prepared under the direction
of an Editorial Board

VOLUME V

Boron

Part A: Boron–Oxygen Compounds

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PREFACE

In general plan, this Supplement follows the one previously published (Volume VIII, Supplement III, *Phosphorus*), except that for reasons arising from bulk of material and convenience of publication the present volume is divided into three separate parts, of which this (Part A) is the first. The Supplement as a whole reflects the rapid and very interesting development of boron chemisty and the related industry since the Second World War. This development is briefly reviewed in the Introduction, which also describes the general arrangement of the three parts.

The publishers have been fortunate in securing the services of a specialist Editor, Professor Raymond Thompson, Research Director of Borax Holdings Limited, to aid the planning and preparation. Professor Thompson's close acquaintance with all branches of boron chemistry during much of its rapid growth has greatly helped towards a discriminating presentation of the large volume of published material. The onerous task of editing this Supplement has been helped by the efficient and conscientious work of Miss Bobbi Gouge of Longman, and her contribution to this volume is gratefully acknowledged.

Efforts have been made to include the most up-to-date material available, although there are slightly different (and indicated) cut-off dates for each Section, as is inevitable with a multi-author treatise covering fields progressing at different rates. Following the precedent established in the *Phosphorus* Supplement, the Editors have not hesitated to include sections on certain appropriate fields of organic boron chemistry, although no attempt has been made to introduce a systematic treatment of organoboron compounds.

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ABBREVIATIONS

absolute	abs.
alternating current	a.c.
ampère-s	amp
Angstrom unit-s	Å
atmosphere-s (after a numeral)	atm
atomic weight	at. wt
boiling point	b.p.
British thermal unit-s	B.Th.U.
Calorie-s (large)	kcal
calorie-s (small)	g-cal
centimetre-s	cm
cubic centimetre-s	cm^3
density (with a numeral)	ρ, d
direct current	d.c.
electromotive force	e.m.f.
foot, feet	ft
freezing point	f.p.
gram-s (with a numeral)	g
hour-s (with a numeral)	hr
inch-es	in.
kilogram-s	kg
kilowatt-s	kW
litre-s (with a numeral)	l
melting point	m.p.
milliampère-s	mA
millilitre-s	ml
millivolt-s	mV
minute-s	min
molecular weight	mol. wt
parts per million	p.p.m.
potential difference	p.d.
second-s (time only)	s
specific gravity	sp. gr.
square centimetre-s	cm^2
vapour density	v.d.
vapour pressure	v.p.
volt-s	V
watt-s	W
wave-length	λ

Abbreviations of Journal titles, etc., in references are listed in Volume VIII, Supplement 1, Nitrogen (Part I), pp. xi–lxviii. A few additional abbreviations have unavoidably been introduced; these conform to current practice in 'Chemical Abstracts'.

INORGANIC BORON CHEMISTRY: AN INTRODUCTION AND BACKGROUND

BY RAYMOND THOMPSON

The inorganic chemistry of boron and its compounds has been the subject of so much attention since the original Volume V of this Treatise was published in 1924 that an entire supplement is now required to cover it. As in other fields of chemistry, most of the information explosion of published papers and patents has occurred since the end of World War II. Greater impetus was given to progress in boron chemistry because of the potential military requirements for certain classes of compounds, which caused more funds to be allocated for research at the universities, in government laboratories and in industry. As a consequence there has been a considerable condensing of the usual time-scale for chemical discovery. This effect is particularly pronounced with the element itself and in the cases of the boron hydrides (boranes) and of the refractory binary compounds formed with most metals and metalloids; and only slightly less so with the boron halides and the alkali–metal borohydrides (or hydroborates) used as intermediates in many preparations of reduced boron compounds. Paradoxically, all of this effort has had little effect or influence on the main boron products industry, in which well over 99% of production tonnage (and probably a similar proportion of sales value) is accounted for by boric acid and its simple inorganic salts, notably borax.[1] Not surprisingly, relatively few of the publications have dealt with this aspect; the field is somewhat less interesting academically and it is not unusual for an industry not to reveal its secrets in print, although some useful review articles have been published.[2–3] It is important that students new to the subject keep the interesting chemistry and the more mundane practical aspect in balanced perspective.[4]

In this Supplement, which is divided into three separately issued Parts, the publishers have endeavoured to cover the field as a whole by inviting specialist authors from the universities and the manufacturing industry to contribute upon the aspects they know best. The sequence of treatment is broadly the same as in the original volume, beginning logically in Part A with occurrence and mineralogy then dealing with the oxygenated compounds, the boron oxides, acids, salts and esters. Part B is devoted to the reduced state and largely covalent compounds containing boron–hydrogen or boron–halogen bonds: the halides, pseudo-halides, hydrides, hydroborates and carboranes. There is also a section describing boron–sulphur and related compounds. The element itself and its refractory binary compounds with carbon, silicon, nitrogen, phosphorus and most metals are dealt with in Part C. Any subdivision of so wide but inter-related an area of chemistry as that of boron and its compounds must to some extent be arbitrary, but the editors believe that the system adopted here is most likely to cater for the needs of both academic and industrial workers in the various fields. It is impossible in any multi-author treatise to ensure that each contribution is similarly up-to-date. Completion dates range from 1968 to 1978 but, where possible, significant new references have been added at proof stage to the earlier contributions. Each Section carries a note at the foot of the opening page on the effective cut-off date for the literature search for that contribution.

The mineralogy of boron sources was well understood at the time of the original Treatise and although many new minerals have been discovered since, they are of minor occurrence and none has achieved commercial significance. The most important discovery, that of a massive deposit of sodium borates in the Mojave Desert of California, was, however, made at about the same time as the original Treatise was published. The era of the research reported in this Supplement thus coincides with this deposit becoming the principal world source of boron chemicals.[1-2] The producer industry has in these years been dominated largely by the RTZ Borax (formerly Borax (Holdings) Limited) group of companies, whose major subsidiary, U.S. Borax & Chemical Corporation, owns and operates the large open-cast sodium borate mine and adjacent refinery at Boron, California (Frontispiece); RTZ Borax controls a similar although much smaller operation in Argentina and was involved in colemanite mining in Turkey. These three geographical locations are the only known places in the world where rich sodium and calcium borate minerals occur, although there are some workable borate ores in parts of Russia and Asia. Second in commercial importance to tincal, $Na_2B_4O_7,10H_2O$, the water-soluble native borax, in solid deposits is the water-insoluble colemanite, $Ca_2B_6O_{11},5H_2O$. Turkey is the main producer, although there is currently something of a renaissance of colemanite mining in California—where the modern-world borate industry began with it a century ago. The fumaroles of Tuscany, volcanic steam jets containing vaporized boric acid, and often mentioned as a boron source in inorganic chemistry textbooks, are no longer of industrial significance. By contrast, lake brines, another somewhat traditional source, are still very important and those of Searle's Lake (also in California) are extracted on an extensive scale using highly developed technology by the other major borate refining company, Kerr–McGee Corporation, in a division which was formerly American Potash and Chemical Corporation.[3] Boron always occurs in fully oxygenated compounds, never as the sulphide or the free element.

The solid ores are invariably won by solid state mining, open-cast methods now being used for sodium borate and conventional underground methods for most of the colemanite.[1] Prior to the working of the California sodium borate deposit (where underground methods were employed for the thirty years up to 1957), borax was obtained either by alkaline decomposition of colemanite or from lake brines. Practically none is now made from colemanite (although some sodium perborate is manufactured via this route). Until the 1973 energy crisis a rising proportion of borax was dehydrated completely by fusion, but the trend subsequently has been towards crystallizing the pentahydrate as major product. Boric acid is almost invariably produced industrially by decomposing the partially or fully refined sodium salt, or the upgraded calcium ore, with sulphuric acid. It is similarly dehydrated to boric oxide by fusion on a large scale. The production interrelationships of the major bulk products of the industry are shown in Fig. 1.[1] The mineralogy, mining and production of borax, boric acid and the alkali metal borates are dealt with in greater detail later in this volume. Borates of other metals, which are extensive in range but are little used, and sodium perborate, which conversely is produced on a vast scale and is one of the major outlets for borax, are also treated fully in separate sections.

It is probable that no other element whose simple salts find such widespread application is itself produced and used in the uncombined form in such insignificant quantities. The total world production of elemental boron is currently estimated to be only of the order of ten tons annually[1], or possibly even less. Two properties account for most of such consumption as there is: the energetics and flame colour of its combustion, which make an impure form useful in flares and military pyrotechnics; and the high stiffness-to-weight ratio of filaments obtained by chemical vapour deposition of a highly pure amorphous form on a suitable substrate used for the reinforcement of light metals and plastics, again primarily for military purposes.

Much has been learned about the structure of the various isomorphs of the element in the course of the militarily inspired research of the past two decades. The same can be said of the metal borides and of boron carbide, nitride, silicide and phosphide. With the exception of the last two, the level of production is in aggregate some two orders of magnitude greater than that of the free element and is growing. Boron carbide, a solid second only to diamond and cubic boron nitride in hardness, has long been employed as an abrasive. It is now also used as a source for boron trichloride and in the 1960s attracted interest as a ceramic armour material. It is produced by the carbothermic reduction of boric oxide. The refractory metal borides and boron alloys are of interest as structural materials for use in aggressive environments and as metallurgical additives. Boron nitride occurs in two main forms: a compound of hexagonal graphitic structure which is relatively soft and finds use as a high-dielectric refractory, and the cubic form with structure, hardness and uses similar to those of diamond.

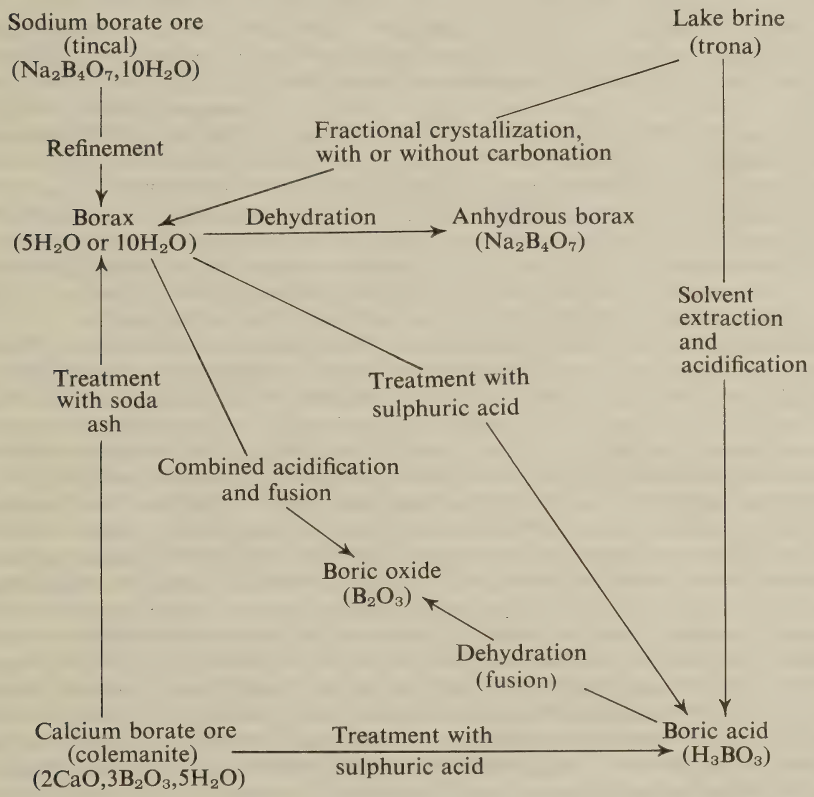

FIG. 1

Boron halides are reviewed in several Sections. The most important commercially is the trifluoride, b.p. −101°C, which finds outlets in catalysis and, in the form of its alkali metal salts (the fluoroborates), as a plating-bath ingredient and metallurgical flux. It is the only boron trihalide made by low-temperature methods, being readily prepared by the action of sulphuric acid upon a mixture of a borate and a fluoride. Boron trichloride, b.p. 12°C, is made on a tonnage scale, primarily for the production of the boron filament referred to above; the favoured route is by the action of chlorine upon boron carbide. Both of these halides are highly reactive and their chemistry is well documented. The sub-halides and pseudo-halides are as yet of academic importance only, although both classes were studied extensively in the post-war search for thermally stable inorganic polymers.

No area of boron chemistry has received so much attention as the boron hydrides, as even a glance at the respective sections of Part B will reveal. Supported during the 1950s and 1960s by large defence contracts, following the initial discoveries of Stock and co-workers[8], and continued by many teams of academic chemists, boron hydride research has contributed a wealth of knowledge about a field analogous to and almost as vast as hydrocarbon chemistry. The military requirements which prompted the research were for a class of fuels of a higher energy than hydrocarbons for use in rocketry and aircraft propulsion. Much of the information developed in the post-war years, until the late 1950s, was consequently subject to security classification, which explains the subsequent surge of publications. These publications in turn had a stimulating effect upon academic workers, who were also helped by the availability of hitherto exotic starting materials. So far as is known the boranes were never used militarily beyond test and experimental firings (although these were often on a large scale) and there is no significant industrial use for the materials. They are powerful reducing agents but the explosion hazard and their high mammalian toxicity preclude their adoption. On the other hand sodium hydroborate (or borohydride), a favoured borane precursor, is fairly readily made and is safe to handle. It possesses selective reducing properties valuable in fields as diverse as the synthesis of fine organic chemicals and the bleaching of newsprint; but it is still too expensive to allow widespread use. The newest and one of the most interesting areas of the borane field is that of the carboranes, first described in the mid-1950s. They are essentially boron cage structures into which carbon atoms, most usually two in number, have been interposed. At least one series of thermally stable polymers based on these compounds is available commercially.[4] The subject is still advancing so rapidly that it has been necessary to add a further bibliography to the contributed carboranes section.

Detailed accounts of the applications of those high-tonnage compounds (borax, boric acid and the like) which constitute the commercially important boron products industry are outside the scope of the present Treatise, but it is appropriate to indicate in broad terms the major uses. They are reviewed from time to time[5, 6], while specific papers from applied science journals, and the many patents, are covered by Chemical Abstracts. Industrial applications of boric acid and the common metal borates (including the up-graded minerals such as colemanite) derive largely from four properties: the glass-forming character of the boron-oxygen unit and its ability upon fusion to enter and modify a silicate network; the nature of borate ions in aqueous media and their counter-effect with cations such as sodium in producing solutions which display chemical buffering; the ability of sodium borate to form the appropriately-stable sodium perborate (of which some 600,000 tons are produced annually as a textile bleach[6]); and the general chemical behaviour of the $\rangle$B–OH groups in a wide range of chemical and biological systems. Such properties render borates valuable, respectively, in the vitreous industries (glass, ceramic glazes, porcelain enamels); as water conditioners for domestic laundering (a major use in the U.S.A.) and numerous industrial processes; as a bleach which is an important ingredient of many packeted washing powders; and for a miscellany of uses both in manufacturing industry and in agriculture.

In the glass and related industries, where the B_2O_3 is taken into vitreous solution, it is often immaterial which source is employed provided that the accompanying metal (if present) is qualitatively and quantitatively compatible with the formulation as a whole. Price in terms of usable B_2O_3 content is often the determining factor, with purity and degree of hydration influencing a premium where these criteria are of technical importance or convenience. For uses in aqueous solution, which are restricted to boric acid and the alkali metal or ammonium borates, the pH of resultant solution is often the deciding factor. For example, it is the mild alkalinity of a borax solution ($pH = 9{\cdot}3$ for a 4·7 per cent solution at 20°C) which renders it both effective as a detergent builder and acceptable to the user in domestic laundering. For uses in timber preservation (boric acid is toxic to many wood-boring insects) and in agriculture (where boron is a vital trace element for many crops), it is particularly fortunate that a mixture of borax and boric acid at a composition approximating to $Na_2O:4B_2O_3$ is at the same time of substantially neutral pH and at a point close to maximum aqueous solubility (9·5% for 20 per cent solution at 20°C), much higher than either substance alone at the same temperature (4·72 per cent for boric acid, 4·71 per cent for borax decahydrate). Mixtures of borax and boric acid have long been known[7] as fire retardants for wood products and other cellulosic materials, an application which in the year 1977 became the largest single use for boric acid.[5] Coincidentally, the same 1:4 ratio of $Na_2O:B_2O_3$ is about the optimum for the dual functions of flameproofing and glowproofing.

By far the largest chemical use for boric acid currently is in connection with organic syntheses. The most important of these, in tonnage terms, is in the petrochemical industry where it is employed to modify the course and selectivity of the liquid phase oxidation of cyclohexane by molecular oxygen to cyclohexanol and cyclohexanone, enabling a better yield of these co-intermediates for nylon production. A similar controlled oxidation of *n*-paraffins is employed in the production of biodegradable detergents. Boric acid is also used industrially in the production of quinalizarin from phthalic anhydride and chlorophenol, and in making salicylaldehyde from phenol and paraformaldehyde.

An application for boron compounds which has little to do with their chemical properties is in the nuclear energy industry. The element boron has two isotopes, ^{10}B and ^{11}B, the natural abundance of the lighter one being about 18·8%. It is, in contrast with ^{11}B, opaque to thermal neutrons (4000 barns) in contact with which it breaks down into lithium and an alpha-particle. Highly purified boric acid is used for pressurized water reactors and in cooling ponds, while boron carbide enriched with respect to $^{10}B_4C$ is employed in control rods, shielding and the like.

With so vast a subject as boron chemistry there have inevitably been many specialist reviews of particular areas, some appearing individually and others collected into textbook or series volume form. Some contributors to the Supplement have indicated such reviews, either as more general reading for students or as related topics not altogether within the scope of the present Treatise. Several compilations are especially noteworthy. Those covering a number of fields include *Borax to Boranes*, edited by P. W. Gilles[9]; *Boron, Metallo-Boron Compounds and Boranes*, edited by R. M. Adams[10]; *The Chemistry of Boron and its Compounds*, edited by E. L. Muetterties[11]; a recent inorganic chemistry reference work[12]; a short simplified textbook by A. G. Massey and J. Kane[13]; and a lengthy compilation by G. V. Samsonov and co-workers.[14] The three volumes of the series *Progress in Boron Chemistry*, edited by R. J. Brotherton, A. L. McCloskey and H. Steinberg[15], contain review chapters covering topics similar to those in this Treatise. Organo-boron chemistry, not quite within the scope of the present work (although short contributions on boric acid esters and boronic and borinic acids have been included), is well reviewed by H. Steinberg and R. J. Brotherton[16] whose scope covers nitrogen-containing organic compounds. *Boron–Nitrogen Compounds* are also described in a book of this title by K. Niedenzu and J. W. Dawson[17] and organic compounds more generally in *The Organic Chemistry of Boron* by W. Gerrard[18] and in a review by K. Niedenzu.[19]

The boranes have been well reviewed in *Boron Hydrides* by W. N. Lipscomb[20]; *Production of the Boranes and Related Research*, edited by R. T. Holzmann[21]; *Polyhedral Boranes* by E. L. Muetterties and W. H. Knoth[22] and in a collection of papers presented at a 1971 symposium.[23] The chemistry of the element itself is well covered in the two symposia volumes, *Boron*, edited by Kohn, Nye and Gaulé[24], by A. E. Newkirk[25], J. G. Bower[26] and by V. I. Matkovich.[27] The chemistry and applications of metal borides have been described by B. Post[28], V. I. Matkovich[27] and R. Thompson.[29,30] The role of boric oxide in glasses is well treated in a recent compilation, *Borate Glasses*, edited by L. D. Pye, V. D. Fréchette and N. J. Kreidl.[31]

The boron compounds supplement of Gmelin's *Handbook of Inorganic Chemistry* was published during the later stages of preparation of the present Treatise.[32]

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SECTION A1

THE MINERALS OF BORON

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The minerals of boron are the naturally occurring compounds (fluoborates, boric acids, borates, compound borates, silicoborates and borosilicates) in which boron is an essential element and is consistently present in amounts of one weight percent, or more, of B_2O_3. By this definition there are about 150 minerals of boron known at present and most of these (92 species) have been described since the publication of the volume on boron (Mellor, V) in 1924. These minerals are listed here in a chemical arrangement and their more important crystallographical, physical and optical properties are tabulated below.

Boron in natural minerals occurs in chemical combination with oxygen (rarely with fluorine) as simple or complex anions. The basic rules governing the nature of of the polyanions found in the fully hydrated borates were formulated by Christ[115, 749 p. 236], as follows:

1. Boron will link either three oxygens to form a triangle or four oxygens to form a tetrahedron;
2. Polynuclear anions are formed by corner sharing only of boron–oxygen triangles and tetrahedra in such a manner that a compact insular group of low to medium negative charge results;
3. In the polyanions of hydrated borates, those oxygens not shared by two [or more (Clark[144])] borons always attach a proton and exist as hydroxyl groups;
4. The insular groups may polymerize in various ways by splitting out water.

A further principle was added by Clark[137]:

5. The boric acid group, $B(OH)_3$, may exist in isolated form in the presence of more complex polyanions, or such insular groups may themselves polymerize and attach as side chains to more complex polyanions.

Predictions, based on these rules, as to the nature of polyanions from the chemical nature of a hydrated borate crystal have been confirmed through subsequent crystal-structure, NMR and infra-red studies[114, 137, 144, 165, 166, 545, 710, 793], and others. These rules apply as well to the hydrated compound borates, silicoborates and borosilicates, and they are the fundamental basis for modern crystallochemical classifications of the boron minerals.

The mechanism of boron substitution for silicon in silicates was discussed by Christ[116]; basically this consists of the replacement of an SiO_4 tetrahedron by a BO_3OH tetrahedron. Under some conditions boron may proxy for tetrahedral aluminium, especially in the more disordered structures[116], but such substitution is only partial in natural minerals.[216, 454] Heier[296] has suggested that ^{10}B may be present in the metamict beryllium-bearing borosilicates as a result of the radioactive decay of ^{10}Be. Boron in three-fold coordination occurs only in four or five silicate minerals: dumortierite[274, 473, 563], grandidierite[345, 473, 563, 649], harkerite[516, 563] and tourmaline.[92, 473, 552, 563] The rare mineral serendibite may have boron in three-fold coordination[552]; however, only tetrahedrally coordinated boron was noted in another study of the infra-red spectra of this mineral.[563] Povarennykh[566] suggested the name 'boratosilicates' for the double compounds of borate and silicate with boron in three-fold coordination.

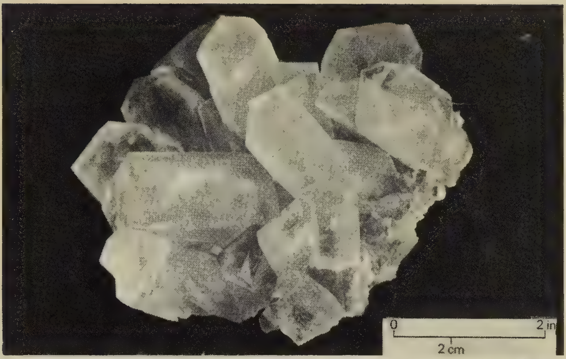
Boron in both three- and four-fold coordination has been found only in the silicoborates. The sole representatives of this class, which have a B:Si ratio greater than one, are the minerals garrelsite[754] and howlite.[236, 475, 476] In the remaining borosilicates, which have B:Si less (usually much less) than one, boron is known only in four-fold coordination. Bakerite, the only borosilicate in which B:Si approaches unity, probably also has tetrahedrally coordinated boron in common with the other members of the datolite group.[119]

Non-essential boron has been found in amounts exceeding one weight percent B_2O_3 in several minerals: as much as 4% B_2O_3 has been noted in idocrase (the variety known as viluite)[98]; other values for boron in idocrase are reported in Table XXIII of Section A2—Boron Geochemistry, this Part; 3·2% B_2O_3 was found in ettringite from Franklin, New Jersey[315], but boron has not been reported in ettringite from other localities[433] nor found to be an essential element in the various crystal-structure determinations of this mineral[65, 159, 482, 483]; up to 1·6% B_2O_3 has been noted in braunite[170, 175, 176, 407, 700] but only a few p.p.m. B have been detected in other occurrences of this mineral.[511] Manganese oxide minerals, other than braunite, generally have a very low content of boron.[170, 299, 300, 571a, 757a] Gadolinite, in which boron is non-essential and ranges from 0·05–4·98%[512], is included in Table I (only) because of its relationship to the datolite group. On the other hand, kornerupine has been synthesized without boron[611], but boron-free kornerupine has not been found as a natural mineral.[304, 346] A few silicates (painite, holtite, and hyalotekite) have quite low B contents and are so rare (each mineral has so far been found in a single occurrence) that their classification as borosilicates is tentative. An extensive list of minerals containing trace amounts of non-essential boron was compiled by Harder.[170]

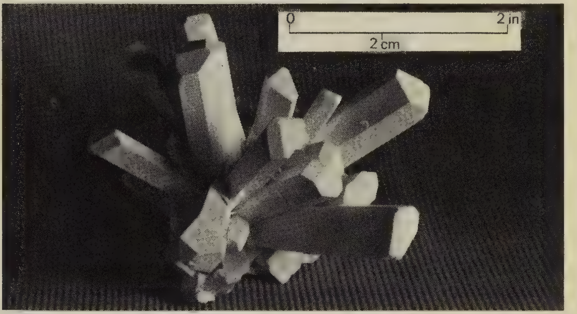
Various classifications have been made of the minerals of boron and of their synthetic analogues. These schemes are based chiefly on arrangement by chemical composition[100, 298, 301, 302, 328, 338, 364–6, 504, 526, 527], by crystal-structure type[115, 126, 308, 580, 583, 652, 664, 673, 708], by combined crystallochemical considerations[74, 564, 566], or by mineral paragenesis.[277, 457] In the Tables (I, II) below, the minerals of boron are arranged chemically into the major groups of fluoborates, boric acids, borates, borates with halogens, compound borates, silicoborates and borosilicates. The simple borates are further arranged, first, by their major cation in the order: Na, Na + Ca, K, NH_4, Be, Mg, Mg + Ca, Ca, Ca + Sr, Sr, Al, Mn, Fe + Mg, Sn and Ta; secondly, by increasing B_2O_3:metal–oxide ratio; and finally, by increasing H_2O content. The borosilicates are also arranged by major (or most important) cation in the order: Li, Na, Ca, Ca + RE, Al, Ba and Pb. The simplified oxide formula for each mineral is given first followed by the structural formula where this is known from crystal-structure studies or has been postulated from other evidence. In general, the formulæ are schematic and ignore minor isomorphic substitution. The oxide formula weight and weight percent B_2O_3 are given for each mineral (for purpose of comparison the B content of the fluoborates is also reported as B_2O_3). The reported range of B_2O_3 is given for some minerals especially for those of complex compositions such as the borosilicates.

Selected crystallographical, physical and optical properties of the boron minerals are given in Table II which follows the same chemical order as Table I. The crystal systems are abbreviated as follows: Triclinic (Tricl), Monoclinic (Monoc), Orthorhombic (Ortho), Hexagonal (Hexag), Rhombohedral (Rhomb), Tetragonal (Tetra), and Cubic. All rhombohedral cells are referred to hexagonal (trigonal) axes. Where the exact space group has not been determined, the symbol of the diffraction aspect[186] has been used to denote a choice between two or more space groups. The unit cells have been re-oriented in some instances to a standard setting[186] and the space group and optical orientation for such minerals have been transformed accordingly. The number in parentheses is the estimated standard deviation referred to the last decimal place. The volume of the unit cell (indicated as V) is given in Å³. The range

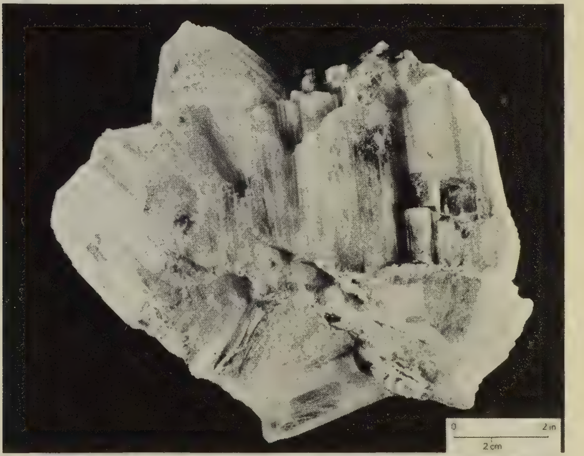
FIG. 1.—Sodium borate minerals



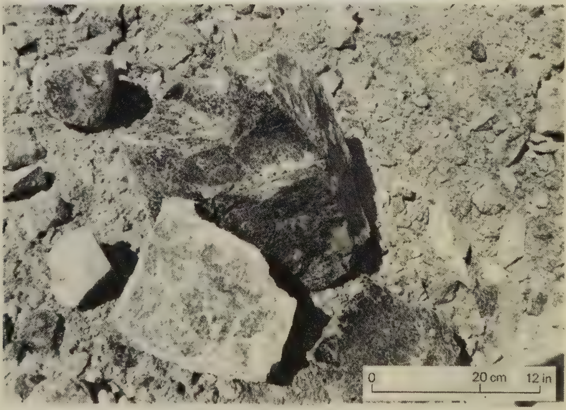
(a)
Tincal, native decahydrate borax
$Na_2B_4O_7 \cdot 10H_2O$
(Boron, California)



(b)
Tincalconite, after borax
$Na_2B_4O_7 \cdot 5H_2O$
(Boron, California)

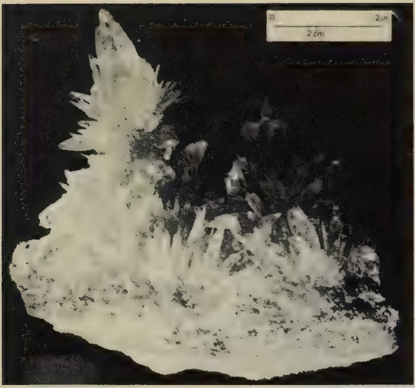


(c)
Kernite, native tetrahydrate borax
$Na_2B_4O_7 \cdot 4H_2O$
(Boron, California)

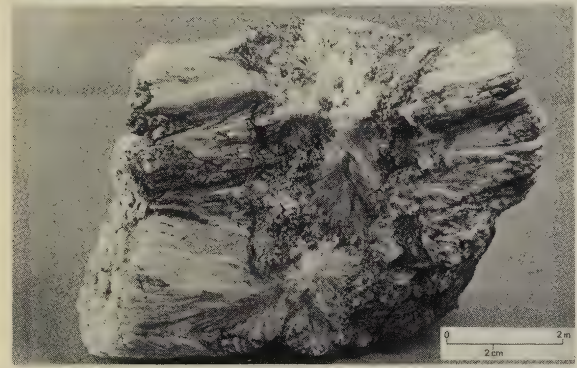


(d)
Tincal, run-of-mine ore
(Boron, California)

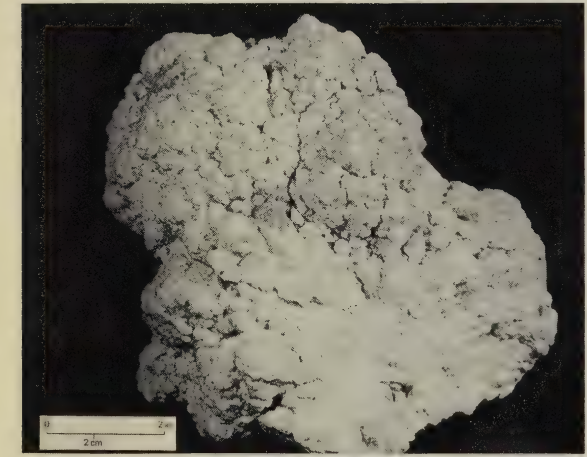
FIG. 2.—Calcium borate minerals



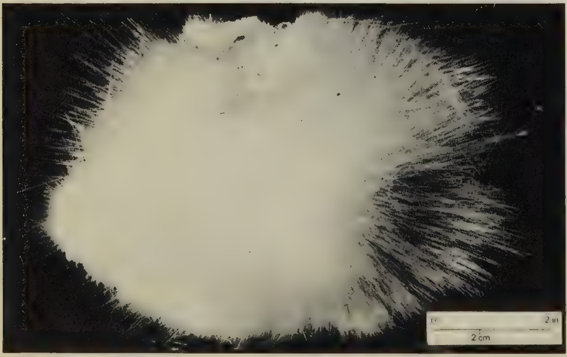
(a)
Colemanite, native calcium borate
$Ca_2B_6O_{11} \cdot 5H_2O$
(Boron, California)



(b)
Colemanite, native calcium borate.
Nodular ore, run-of-mine
$Ca_2B_6O_{11} \cdot 5H_2O$
(Turkey)



(c)
Ulexite, native sodium–calcium borate.
Nodular or ‘cauliflower’ form
$Na_2Ca_2B_{10}O_{18} \cdot 16H_2O$
(Boron, California)



(d)
Ulexite, native sodium–calcium borate.
‘Bunny-tail’ form
$Na_2Ca_2B_{10}O_{18} \cdot 16H_2O$
(Boron, California)

in value of a parameter reported for some minerals, or for some mineral series, is given for the minimal and maximal values of each parameter so that the corresponding unit-cell volumes represent presently known limiting values. In some cases (e.g. leucosphenite) these limits lead to unit-cell volumes that slightly exceed reported values.[770] This is most noticeable in the borosilicate group of minerals where isomorphous substitution is of more importance.

The number of structural formulæ per unit cell (or of oxide formulæ per unit cell in a relatively few instances where the crystal structure has not been determined) is denoted by Z. Densities were calculated using the cell volumes and oxide formula weights (Table I) and take no account of substitution in formulæ except for end-members of a mineral series. Natural minerals and synthetic compounds are represented by (n) or (s) respectively. Indexed X-ray powder data are indicated by an asterisk (*) followed by an 'n' or 's' to indicate natural minerals or their synthetic equivalents; data for the latter are generally given where information for both were available.

Optical properties given here are the optical group, indices of refraction, axial angle (2V), colour in transmitted light, optical orientation and dispersion. Pleochroic schemes are noted under colour. The optical orientation is not given for most of the triclinic minerals, but may be found in the references cited. The sign of the extinction angle is given as reported in the original reference; it is not always clear which convention has been followed by a particular author. Mineral hardness is given on the Mohs' scale; values obtained by microindentation have been converted to this scale.

The minerals of boron have been arranged in alphabetic order in Table III and may be quickly located in Table I (and then Table II) by using the generalized composition given for each mineral. A list of synonyms and varietal, obsolete, or misspelled names of the boron minerals has been compiled from various sources[103, 301, 302, 380, 526, 527, 564–6, 652, 673, 796, 807], and others, and is given as Table IV. Several misspelled names are given because many of them have appeared frequently as transliterations from Russian or Chinese literature (often passing into English through an intermediate translation from German as in the instance of hungchaoite). The preferred mineral name is capitalized in both of Tables III and IV.

The occurrences of the geochemically important boron minerals may be found in Section A2—Boron Geochemistry (this Part). Other data on the minerals of boron are given in the following selected references. Most of the data for the following subjects consist of values too lengthy to tabulate here. The list of references is not exhaustive, but the more recent and more general papers have been chosen and most of these contain references to the earlier literature.

Differential thermal analysis:	11, 53, 128, 218–23, 326, 335, 354, 361, 507, 619, 680, 681
Fluorescence (ultraviolet):	709, 755
Fluorescence (infra-red):	34
Spectra	
Optical absorption:	213, 226, 337, 551, tourmaline: 78, 227, 447, 448, 577, 679, 695, 716, 756, 757, 763
Infra-red (borates):	4, 7, 298, 314, 367, 416, 469–72, 474, 475, 476, 505, 507, 552, 562, 563, 664, 685, 686, 689 710–12, 742, 775
Infra-red (borosilicates):	9, 36, 51, 260, 313, 343, 390, 475, 476, 552, 553, 558, 560, 561, 563, 774, 775
Raman:	44, 152, 281, 282, 496
Nuclear magnetic resonance:	5, 64, 69, 84, 160–2, 298, 321, 375, 376, 404, 405, 451, 478, 545, 546, 580, 597, 632, 633, 706, 713, 721, 722, 740, 771
Nuclear quadrupole resonance:	71, 758
Electron paramagnetic resonance:	25, 54–60, 413, 508, 760
Mössbauer:	8, 214, 445, 610, 662, 734, 745, 765

Table I.—The Minerals of Boron arranged Chemically

Major cation	Mineral	Oxide formula	Structural formula	Oxide formula weight	B_2O_3 (Wt. %)	%B_2O_3 (reported range)	Reference
	Fluoborates						
Na	Ferruccite	$NaBF_4$	$Na[BF_4]$	109·79	31·70		90, 713
K	Avogadrite	$(K, Cs)BF_4$	$(K, Cs)[BF_4]$	125·91	27·64		89, 151
	Boric Acid						
	Sassolite (orthoboric acid)	$B_2O_3.3H_2O$	$B(OH)_3$	123·67	56·29		808
	Metaborite (metaboric acid)	$B_2O_3.H_2O(\gamma)$	$BO(OH)$	87·64	79·44		425, 727
	Borates						
Na	Kernite[a]	$Na_2O.2B_2O_3.4H_2O$	$Na_2[B_4O_6(OH)_2].3H_2O$	273·28	50·95		127, 156, 268, 794
	Tincalconite[a]	$Na_2O.2B_2O_3.5H_2O$	$Na_2[B_4O_5(OH)_4].3H_2O$	291·30	47·80		545, 789
	Borax[a]	$Na_2O.2B_2O_3.10H_2O$	$Na_2[B_4O_5(OH)_4].8H_2O$	381·38	36·51		266, 487
	Biringuccite	$2Na_2O.5B_2O_3.3H_2O$	$Na_4[B_{10}O_{16}(OH)_2].2H_2O$	526·11	66·16		129–31, 809
	Nasinite	$2Na_2O.5B_2O_3.5H_2O$	$Na_2[B_5O_8(OH)].2H_2O$	562·14	61·92		129, 130, 211, 814
	Ezcurrite	$2Na_2O.5B_2O_3.7H_2O$	$Na_2[B_5O_7(OH)_3].2H_2O$	598·16	58·20		316, 746
	Ameghinite	$Na_2O.3B_2O_3.4H_2O$	$Na[B_3O_3(OH)_4]$	342·90	60·91		19, 815
	Aristarainite	$Na_2O.MgO.6B_2O_3.H_2O$		700·16	59·66		810
	Rivadavite	$3Na_2O.MgO.12B_2O_3.22H_2O$	$Na_6Mg[B_6O_7(OH)_6]_4.10H_2O$	1458·04	57·30		320, 785
	Sborgite	$Na_2O.5B_2O_3.10H_2O$	$Na[B_5O_6(OH)_4].3H_2O$	590·24	58·98		132, 766
Na & Ca	Probertite	$Na_2O.2CaO.5B_2O_3.10H_2O$	$NaCa[B_5O_7(OH)_4].3H_2O$	702·40	49·57		587
	Ulexite[b]	$Na_2O.2CaO.5B_2O_3.16H_2O$	$NaCa[B_5O_6(OH)_6].5H_2O$	810·50	42·95		146
	Braitschite	$6(Ca, Na_2)O.RE_2O_3.12B_2O_3.6H_2O$ (?)				48·2	571
K	Santite	$K_2O.5B_2O_3.8H_2O$	$K[B_5O_6(OH)_4].2H_2O$	586·42	59·36		463, 731
NH_4	Larderellite	$(NH_4)_2O.5B_2O_3.4H_2O$	$NH_4[B_5O_7(OH)_2].H_2O$	472·24	73·71		462
	Ammonioborite	$3(NH_4)_2O.15B_2O_3.16H_2O$	$(NH_4)_3[B_{15}O_{20}(OH)_8].4H_2O$	1488·78	70·14		142, 461
Be	Hambergite	$4BeO.B_2O_3.H_2O$	$Be_2(OH)[BO_3]$	187·68	37·10		645, 730
	Berborite	$4BeO.B_2O_3.3H_2O$	$Be_2(OH)[BO_3].H_2O$	223·71	31·12		609
	Rhodizite	$Cs_2O.8BeO.4Al_2O_3.11B_2O_3.2H_2O$	$CsBe_4Al_4B_{11}O_{26}(OH)_2$	1691·58	45·27		91, 184, 671
Mg	Wightmanite	$10MgO.B_2O_3.8H_2O$	$Mg_5O(OH)_5[BO_3].nH_2O$	616·84	12·08		486, 493
	Kotoite	$3MgO.B_2O_3$	$Mg_3[BO_3]_2$	190·55	36·54		593, 594
	Suanite	$2MgO.B_2O_3$	$Mg_2[B_2O_5]$	150·24	46·34		666

[a] See Fig. 1; [b] See Fig. 2.

Table I.—(*continued*)

Major cation	Mineral	Oxide formula	Structural formula	Oxide formula weight	B_2O_3 (Wt. %)	%B_2O_3 (reported range)	Reference
	Szaibelyite	$2MgO.B_2O_3.H_2O$	$Mg_2(OH)[B_2O_4(OH)]$	168·26	41·38		538
	Pinnoite	$MgO.B_2O_3.3H_2O$	$Mg[B_2O(OH)_6]$	163·98	42·46		377, 532
	Inderite	$2MgO.3B_2O_3.15H_2O$	$Mg[B_3O_3(OH)_5].5H_2O$	559·72	37·32		585
	Kurnakovite	$2MgO.3B_2O_3.15H_2O$	$Mg[B_3O_3(OH)_5].5H_2O$	559·72	37·32		572, 723
	Preobrazhenskite	$6MgO.11B_2O_3.9H_2O$	$Mg_3[B_{11}O_{14}(OH)_8].H_2O$	1169·82	65·46		518, 586
	Halurgite	$2MgO.4B_2O_3.5H_2O$		449·18	62·00		350
	Hungchaoite	$MgO.2B_2O_3.9H_2O$	$Mg[B_4O_4(OH)_6].6H_2O$	341·69	40·75		1, 2, 3, 123
	Kaliborite	$K_2O.4MgO.12B_2O_3.19H_2O$	$HKMg_2[B_6O_8(OH)_5]_2.4H_2O$	1433·18	58·29		157, 158
	Aksaite	$MgO.3B_2O_3.5H_2O$	$Mg[B_6O_7(OH)_6].2H_2O$	339·25	61·57		165, 290
	Mcallisterite	$2MgO.6B_2O_3.15H_2O$	$Mg_2[B_6O_7(OH)_6]_2.9H_2O$	768·58	54·35		166
Mg & Ca	Hydroboracite	$CaO.MgO.3B_2O_3.6H_2O$	$CaMg[B_3O_4(OH)_3]_2.3H_2O$	413·35	50·53		584
	Inderborite	$CaO.MgO.3B_2O_3.11H_2O$	$CaMg[B_3O_3(OH)_5]_2.6H_2O$	503·43	41·49		392–397
	Kurchatovite	$6CaO.5MgO.MnO.6B_2O_3$	$Ca_6Mg_5Mn[B_2O_5]_6$	1026·69	40·69		440, 506
	Wardsmithite	$5CaO.MgO.12B_2O_3.30H_2O$		1696·63	49·24		212
Ca	Sibirskite	$2CaO.B_2O_3.H_2O$ (?)		199·80	34·85		687
	Olshanskyite	$3CaO.2B_2O_3.9H_2O$	$Ca_3(OH)_2[B(OH)_4]_4$	469·62	29·65		73
	Calciborite	$CaO.B_2O_3$ (II)	$Ca[B_2O_4]$	125·70	55·39		450, 624, 728
	Korzhinskite	$CaO\cdot B_2O_3.H_2O$		143·72	48·44		439, 623
	Uralborite	$CaO.B_2O_3.2H_2O$	$Ca[B_2O_2(OH)_4]$	161·73	43·05		626
	Vimsite	$CaO.B_2O_3.2H_2O$	$Ca[B_2O_2(OH)_4]$	161·73	43·05		627
	Nifontovite	$3CaO.3B_2O_3.8H_2O$	$Ca_3[B_3O_3(OH)_6]_2.2H_2O$	521·23	40·07		441, 787
	Frolovite	$CaO.B_2O_3.4H_2O$ (β)	$Ca[B(OH)_4]_2$	197·76	35·20		200, 548, 733
	Pentahydroborite	$CaO.B_2O_3.5H_2O$	$Ca[B_2O(OH)_6].2H_2O$	215·78	32·26		443, 623, 782, 817
	Tyretskite	$4CaO.5B_2O_3.3H_2O$ (?)	$Ca_2(OH)[B_5O_8(OH)_2]$ (?)	626·47	55·57		169, 354
	Priceite	$4CaO.5B_2O_3.7H_2O$		698·53	49·83		369
	Tertschite	$4CaO.5B_2O_3.20H_2O$		932·74	37·32		458, 459
	Fabianite	$2CaO.3B_2O_3.H_2O$	$Ca[B_3O_5(OH)]$	339·04	61·60		210, 254, 357
	Colemanite†	$2CaO.3B_2O_3.5H_2O$	$Ca[B_3O_4(OH)_3].H_2O$	411·10	50·81		117, 138
	Meyerhofferite	$2CaO.3B_2O_3.7H_2O$	$Ca[B_3O_3(OH)_5].H_2O$	447·13	46·71		120, 138
	Inyoite	$2CaO.3B_2O_3.13H_2O$	$Ca[B_3O_3(OH)_5].4H_2O$	555·23	37·62		138, 140
	Volkovskite	(Ca, Sr)$O.3B_2O_3.3H_2O$		318·90^a	65·48	57·0–65·5	355
	Nobleite	$CaO.3B_2O_3.4H_2O$	$Ca[B_6O_9(OH)_2].3H_2O$	337·00	61·98		145
	Gowerite	$CaO.3B_2O_3.5H_2O$	$Ca[B_5O_8(OH).B(OH)_3].3H_2O$	355·02	58·83		115, 358

† See Fig. 2.

Table I.—(continued)

Major cation	Mineral	Oxide formula	Structural formula	Oxide formula weight	B_2O_3 (Wt. %)	$\%B_2O_3$ (reported range)	Reference
	Ginorite	$2CaO.7B_2O_3.8H_2O$	$Ca_2[B_{14}O_{20}(OH)_6].5H_2O$	743·63	65·54		360
Ca	Kurgantaite	$2(Sr, Ca)O.2B_2O_3.H_2O$		316·96^{a}	43·93	41·41	354, 719
&	Unnamed mineral	$(Ca, Sr)O.B_2O_3.H_2O$ (?)		167·49	41·57		693
Sr	Strontioborite	$SrO.4B_2O_3.2H_2O$	$Sr[B_8O_{11}(OH)_4]$	418·13	66·60		352, 426, 813
	Strontioginorite	$SrO.CaO.7B_2O_3.8H_2O$	$SrCa[B_{14}O_{20}(OH)_6].5H_2O$	791·17	61·60		360
Sr	Veatchite	$4SrO.11B_2O_3.7H_2O$	$Sr_2[B_5O_8(OH)]_2.B(OH)_3.H_2O$	1306·41	58·62		149, 150
	p-Veatchite	$4SrO.11B_2O_3.7H_2O$	$Sr_2[B_5O_8(OH)]_2.B(OH)_3.H_2O$	1306·41	58·62		257, 588, 589
	Tunellite	$SrO.3B_2O_3.4H_2O$	$Sr[B_6O_9(OH)_2].3H_2O$	384·54	54·31		144
Al	Johachidolite	$2CaO.Al_2O_3.3B_2O_3$	$CaAl[B_3O_7]$	422·98	49·38		327, 767
	Sinhalite	$2MgO.Al_2O_3.B_2O_3$	$MgAl[BO_4]$	252·20	27·61		225
	Jeremejevite	$6Al_2O_3.5B_2O_3.3H_2O$	$Al_6[B_5O_{15}(OH)_3]$	1013·91	34·33		275, 574
Mn	Pinakiolite	$3MgO.MnO.Mn_2O_3.B_2O_3$	$(Mg, Mn^{2+})_2Mn^{3+}O_2[BO_3]$	419·36	16·60		668
	Orthopinakiolite	$3MgO.MnO.Mn_2O_3.B_2O_3$	$(Mg, Mn^{2+})_2Mn^{3+}O_2[BO_3]$	419·36	16·60		570
	Wiserite	$4MnO.B_2O_3.2H_2O$	$Mn_4(OH)_4[B_2O_5]$	389·41	17·88		206, 673
	Jimboite	$3MnO.B_2O_3$	$Mn_3[BO_3]_2$	282·44	24·65		593
	Sussexite	$2MnO.B_2O_3.H_2O$	$Mn_2(OH)[B_2O_3(OH)]$	229·52	30·33		88, 538
	Roweite	$2CaO.2(Mn, Mg)O.2B_2O_3.3H_2O$	$Ca_2(Mn, Mg)_2(OH)_4[B_4O_7(OH)_2]$	447·33^{b}	31·13		442, 792, 793
	Unnamed mineral ('Mineral X')	Manganese borate					206
Fe	Warwickite	$3(Mg, Fe)O.TiO_2.B_2O_3$	$(Mg, Fe^{2+})_3TiO_2[BO_3]_2$	270·45^{c}	25·74		93, 668
&	Ludwigite	$4(Mg, Fe)O.Fe_2O_3.B_2O_3$	$(Mg, Fe^{2+})_2Fe^{3+}O_2[BO_3]$	390·56^{d}	17·83	14·00–18·29	6, 479, 480, 765
Mg	Azoproite	$4(Mg, Fe)O.(Fe, Ti, Mg)_2O_3.B_2O_3$	$(Mg, Fe^{2+})_2(Fe^{3+}, Ti, Mg)O_2[BO_3]$			19·07	356
	Vonsenite	$4(Fe, Mg)O.Fe_2O_3.B_2O_3$	$(Fe^{2+}, Mg)_2Fe^{3+}O_2[BO_3]$	516·71^{e}	13·47	12·38–16·16	6, 229, 479, 480, 765
	Hulsite	$4(Fe, Mg)O.(Fe, Sn)_2O_3.B_2O_3$	$(Fe^{2+}, Mg)_2(Fe^{3+}, Sn^{4+})O_2[BO_3]$			9·53–13·20	139, 359
Ni	Bonaccordite	$4NiO.Fe_2O_3.B_2O_3$	$Ni_2Fe^{3+}O_2[BO_3]$	528·15	13·18		816
Sn	Nordenskiöldine	$CaO.SnO_2.B_2O_3$	$CaSn[BO_3]_2$	276·39	25·19		201, 729
Ta	Behierite	$(Ta, Nb)_2O_5.B_2O_3$	$(Ta, Nb)[BO_4]$	511·51^{f}	13·61		488
	Borates with Halogens						
	Teepleite	$Na_2O.2NaCl.B_2O_3.4H_2O$	$Na_2Cl[B(OH)_4]$	320·54	21·72		241, 242
	Bandylite	$CuO.CuCl_2.B_2O_3.4H_2O$	$CuCl[B(OH)_4]$	335·68	19·57		153
	Satimolite	$KCl.2NaCl.2Al_2O_3.3B_2O_3.13H_2O$	$KNa_2Al_4Cl_3[B_2O_5]_3{\cdot}13H_2O$	838·43	24·91		517

Table I.—(continued)

Major cation	Mineral	Oxide formula	Structural formula	Oxide formula weight	B_2O_3 (Wt. %)	%B_2O_3 (reported range)	Reference
	Ivanovite	Hydrous chloroborate of Ca (and K?)					347
	Fluoborite	$3MgO.3Mg(OH, F)_2.B_2O_3$	$Mg_3(OH, F)_3[BO_3]$	371·50^a	18·74	17·38–18·68	237, 665
	Boracite	$5MgO.MgCl_2.7B_2O_3$ (α)	$Mg_3Cl[B_7O_{13}]$	784·11	62·15		752, 786, 790
	Ericaite	$5FeO.FeCl_2.7B_2O_3$(α)	$Fe_3Cl[B_7O_{13}]$	973·34	50·07		379, 752, 786
	Congolite	$5FeO.FeCl_2.7B_2O_3$ (Trigonal)	$Fe_3Cl[B_7O_{13}]$	973·34	50·07		714, 752, 786
	Chambersite	$5MnO.MnCl_2.7B_2O_3$(α)	$Mn_3Cl[B_7O_{13}]$	967·88	50·35		307
	Chelkarite	$4CaO.3MgO.3MgCl_2.4B_2O_3.26H_2O$ (?)		1377·80	20·21		23, 781
	Hydrochlorborite	$3CaO.CaCl_2.4B_2O_3.22H_2O$		954·06	29·19		112, 113
	Hilgardite	$3CaO.CaCl_2.5B_2O_3.2H_2O$	$Ca_2Cl[B_5O_8(OH)_2]$	663·36	52·48		82
	Parahilgardite	$3CaO.CaCl_2.5B_2O_3.2H_2O$	$Ca_2Cl[B_5O_8(OH)_2]$	663·36	52·48		82
	Strontiohilgardite	$3(Sr, Ca)O.(Sr, Ca)Cl_2.5B_2O_3.2H_2O$	$SrCaCl[B_5O_8(OH)_2]$	758·43^a	45·90		82
	Solongoite	$7CaO.CaCl_2.6B_2O_3.9H_2O$	$Ca_4Cl[B_6O_8(OH)_9]$	1083·40	38·56		811
	Aldzhanite	Hydrous (?) chloroborate of Ca and Mn				23·6	23
	(See also: Sakhaite, heidornite, sulfoborite.)						
	Borates with Carbonate						
	Sakhaite	$48CaO.14MgO.2MgCl_2.16CO_2.14B_2O_3.8H_2O$	$Ca_{48}Mg_{16}(OH)_8Cl_4[CO_3]_{16}[BO_3]_{28}.4H_2O$	5269.58	18·50		516
	Carboborite	$2CaO.MgO.CO_2.B_2O_3.10H_2O$	$Ca_2Mg[CO_3][B_2O_3(OH)_4].8H_2O$	446·26	15·60		309
	Borcarite	$4CaO.MgO.2CO_2.2B_2O_3.3H_2O$	$Ca_4Mg[CO_3]_2[B_4O_6(OH)_6]$	545·94	25·50		644
	Gaudefroyite	$8CaO.3MnO_3.2CO_2.3B_2O_3$	$Ca_4Mn_3O_3[CO_3][BO_3]_3$	1219·13	17·13		280
	Borates with Phosphate or Arsenate						
	Cahnite	$4CaO.As_2O_5.B_2O_3.4H_2O$	$Ca_2[AsO_4][B(OH)_4]$	595·84	11·68		567
	Teruggite	$4CaO.MgO.As_2O_5.6B_2O_3.20H_2O$	$Ca_4Mg[AsB_6O_{11}(OH)_6]_2.14H_2O$	1272·51	33·78		22, 167
	Lüneburgite	$3MgO.P_2O_5.B_2O_3.8H_2O$	$Mg_3[PO_4]_2[B_2O(OH)_4].6H_2O$	476·62	14·61		80
	Seamanite	$6MnO.P_2O_5.B_2O_3.6H_2O$	$Mn_3^{2+}(OH)_2[B(OH)_4(PO_4)]$	745·30	9·34		370, 398, 485
	Borates with Sulphate						
	Heidornite	$Na_2O.2NaCl.6CaO.4SO_3.5B_2O_3.2H_2O$	$Na_2Ca_3Cl[SO_4]_2[B_5O_8(OH)_2]$	1219·73	28·54		96, 97
	Sulfoborite	$2MgO.Mg(OH, F)_2.SO_3.B_2O_3.4H_2O$	$Mg_3(OH)F[SO_4][B(OH)_4]_2$	362·68	19·20	19·2–19·8	267, 520
	Silicoborates						
	Howlite	$4CaO.2SiO_2.5B_2O_3.5H_2O$	$Ca_2[B_3O_4(OH)_2SiB_2O_5(OH)_3]$	782·66	44·48		236

Table I.—(continued)

Major cation	Mineral	Oxide formula	Structural formula	Oxide formula weight	B_2O_3 (Wt. %)	%B_2O_3 (reported range)	Reference
	Garrelsite	$Na_2O.6BaO.4SiO_2.7B_2O_3.4H_2O$	$NaBa_3[Si_2B_7O_{16}(OH)_4]$	1781·74	27·35		754, 791
	Borosilicates						
Li	Manandonite	$Li_2O.5Al_2O_3.B_2O_3.4SiO_2.8H_2O$	$LiAl_4[AlBSi_2O_{10}(OH)_8]$	993·75	7·01		105, 566
Na	Tourmaline (Group)	$Na_2O.6RO.6Al_2O_3.3B_2O_3.12SiO_2.4(H_2O, F)$ (dravite type)					
	Elbaite		$Na(Li, Al)_3Al_6(OH, F)_4[BO_3]_3[Si_6O_{18}]$	1897·09^{g}	11·01	7·26–11·54	672, 694, 751
	Dravite		$NaMg_3Al_6(OH, F)_4[BO_3]_3[Si_6O_{18}]$	1917·48^{h} 1921·41^{i}	10·89 10·87	4·61–11·78	92, 185, 672, 677, 697
	Schorl		$Na(Fe^{3+}, Mn^{3+})_3Al_6(OH, F)_4[BO_3]_3[Si_6O_{18}]$	2154·69^{e,h}	9·69	6·61–11·46	185, 672, 677, 694
	Tsilaisite	(Hypothetical end-member)	$NaMn_3Al_6(OH, F)_4[BO_3]_3[Si_6O_{18}]$	1050·63^{h}	9·94		386, 636, 652, 672, 677
	Uvite	(Hypothetical end-member)	$CaMg_3(Al_5Mg)(OH, F)_4[BO_3]_3[Si_6O_{18}]$	973·16^{h}	10·73		386, 652, 672
	Buergerite		$NaFe_3^{3+}Al_6O_3(F, OH)[BO_3]_3[Si_6O_{18}]$			10·86–11·5	42, 672, 676
	Reedmergnerite	$Na_2O.B_2O_3.6SiO_2$	$Na[BSi_3O_8]$	492·08	14·15		17
	Searlesite	$Na_2O.B_2O_3.4SiO_2.2H_2O$	$Na[BSi_2O_5[OH]_2]$	407·95	17·07		372
Ca	Datolite (Group)						
	Datolite	$4CaO.2B_2O_3.4SiO_2.2H_2O$	$Ca_4[B_4(SiO_4)_4(OH)_4]$	639·91	21·76		119, 530, 533, 656, 788
	'Mineral A'	$2CaO.Y_2O_3.2BeO.B_2O_3.4SiO_2.2H_2O$	$Ca_2Y_2[Be_2B_2(SiO_4)_4(OH)_4]$				191, 615
	Bakerite	$8CaO.5B_2O_3.6SiO_2.5H_2O$	$Ca_4[B_4(SiO_4)_3(BO_3OH)(OH)_4]$	1247·30	27·91		119
	Homilite	$4CaO.2FeO.2B_2O_3.4SiO_3$	$Ca_4Fe_2[B_4(SiO_4)_4O_4]$	747·58	18·63		652
	Gadolinite	$2Y_2O_3.2FeO.4(BeO, B_2O_3).4SiO_2$	$Y_4Fe_2[(Be, B)_4(SiO_4)_4O_4]$			0–4·98	9, 533
	Danburite	$CaO.B_2O_3.2SiO_2$	$Ca[BSiO_4]_2$	245·86	28·32		330, 773
	Axinite (Group)	$6(Ca, Mn, Fe^{2+})O.2Al_2O_3.B_2O_3.8SiO_2.H_2O$	$(Ca, Mn, Fe^{2+})_3Al_2[Si_2O_6][Si_2O_6BO_3(OH)]$	Variable	Variable	1·59–7·62	324
	Ferroaxinite		$Ca_2FeAl_2[Si_2O_6][Si_2O_6BO_3(OH)]$	1140·22	6.11		596
	Manganaxinite		$Ca_2MnAl_2[Si_2O_6][Si_2O_6BO_3(OH)]$	1138·40	6·12		596

Table I.—(continued)

Major cation	Mineral	Oxide formula	Structural formula	Oxide formula weight	B_2O_3 (Wt. %)	%B_2O_3 reported range)	Reference
	Tinzenite		$(Ca, Mn)_2MnAl_2[Si_2O_6)[Si_2O_6BO_3(OH)]$	1168·11	5·96		596
	Harkerite	$96CaO.30MgO.2MgCl_2.3Al_2O_3.36CO_2.15B_2O_3.24SiO_2.12H_2O$	$Ca_{48}Mg_{16}Al_3(OH)_6Cl_2[CO_3]_{18}[BO_3]_{15}[SiO_4]_{12}.3H_2O$	11376·07	9·18		516
Ca & RE	Melanocerite		$CaRE_4BSi_3O_{14}(F, OH)$			0·05–4·85	784
	Caryocerite		$(Ca, Na)_4(RE, Th, Ce)_6[(Si, B)O_4]_6F_2.5H_2O$			1·50–4·70	389
	Tritomite		$(Ca, Na)_4(RE, Th)_6[(Si, B)O_4]_6F_2.6H_2O$			7·31–8·37	389
	Spencite		$(RE, Ca)_6(B, Al)_4[(Si, B)O_4]_6(OH, F)_2.8H_2O$			10·04–11·12	389
			$(RE, Ca)_3(Al, Fe)B_2(Si, Al)_3(O, OH, F)_{15}.nH_2O$				77
	Stillwellite	$(Ce, La)_2O_3.B_2O_3.2SiO_2$	$(Ce, La)BO[SiO_4]$	516·80[a]	13·47	10·4–13·5	501, 691
	Hellandite	$2(Ca, Y)O.3(Si, B, Al)O_2.H_2O$	$(Ca, Y)_2(Si, B, Al)_3O_8.H_2O$			8·47–14·47	306
	Tadzhikite	$3CaO.(Ce, Y)_2O_3.(Ti, Al, Fe)O_2.2B_2O_3.4SiO_2$	$Ca_3(Ce, Y)_2(Ti, Al, Fe)B_4Si_4O_{22}$	995·95	14·57	12·70–14·47	199
	Cappelenite	$6(Ba, Ca, Ce)O.3(Y, Ce, La)_2O_3.6B_2O_3.3SiO_2$	$(Ba, Ca, Ce)_3(Y, Ce, La)_3[(BO_3)_6Si_3O_9]$			16·88–17·16	652
Al	Painite	$4CaO.10Al_2O_3.(2SiO_2, B_2O_3).H_2O$	$5Al_2O_3.Ca_2[(Si, BH)O_4]$			2.2	134, 652
	Serendibite	$10(Ca, Mg)O.5Al_2O_3.B_2O_3.6SiO_2$	$(Ca, Mg)_5(AlO)_5[BO_3(SiO_4)_3]$	1421·85[a]	4·90	4·17–8·61	652, 655
	Grandidierite	$2(Mg, Fe)O.3Al_2O_3.B_2O_3.2SiO_2$	$(Mg, Fe)Al_3[BO_3(SiO_4)O_2]$	607·82[a]	11·45	2·81–11·57	345, 649
	Kornerupine	$12MgO.14Al_2O_3.B_2O_3.14SiO_2.2H_2O$	$Mg_3Al_6O_4(OH)[Si_2O_7][(Al Si)_2(Si, B)O_{10}]$	2857·93	2·44	1·92–3·59	41, 289, 346, 484
	Dumortierite	$7(Al, Fe)_2O_3.B_2O_3.6SiO_2$	$(Al, Fe)_7O_3[(BO_3)(SiO_4)_3]$	1143·82	6·09	1·60–5·37	133, 274
	Holtite	$7(Al, Sb, Ta)_2O_3.B_2O_3.6SiO_2(?)$				1·82	568
Ba	Tienshanite	$Na_2O.BaO.MnO.TiO_2.B_2O_3.6SiO_2$		796·26	8·74		194
	Leucosphenite	$2Na_2O.BaO.2TiO_2.B_2O_3.10SiO_2$	$Na_4BaTi_2O_2[B_2Si_{10}O_{28}]$	1107·52	6·29		106, 629, 630, 770
Pb	Hyalotekite	$8(Pb, Ca, Ba)O.B_2O_3.12SiO_2(F_2, H_2O)$	$(Pb, Ca, Ba)_4(F, OH)[(BO_3)Si_6O_{14}]$			3·73	63, 652

[a] Calculated for 1:1 substitution in oxide formula; [b] Mn end member; [c] Calculated for no Fe; [d] Mg end member; [e] Fe end member; [f] Ta end member; [g] Calculated for 2Li:Al and all OH; [h] All OH; [i] All F.

Table II.—*The Minerals of Boron: Crystallographical, Physical and Optical Properties*

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
Fluoborates												
Ferruccite	Ortho	*a*	6·7916(4)	4	2·5075	2·496	3·39	(100)*s	Biax (+)	X=*b*	3(?)	90, 99, 713, 795
		b	6·8368(9)		(s)	(s)	3·41	(85)	α 1·301	Y=*a*		
	Amam	*c*	6·2619(7)				2·31	(40)	β 1·3012(calc.)	Z=*c*		
							2·84	(25)	γ 1·3068			
		V	290·76				3·82	(20)	2V 11° 25′			
							2·14	(20)	colourless			
Avogadrite	Ortho	*a*	7·0299(8)	4	2·5067	2·50	3·41	(100)*s	Biax (−)	X=*a*	(?)	89, 151, 527, 795
		b	8·6588(5)		(s)	(s)	3·26	(80)	α 1·3239	Y=*c*		
	Pbnm	*c*	5·4800(5)				3·06	(75)	β 1·3245	Z=*b*		
							2·068	(55)	γ 1·3247			
		V	333·57				3·51	(45)	2V very large (?)			
							2·801	(40)	colourless to			
									white, yellow			
Boric Acid												
Sassolite	Tricl	*a*	7·039(1)	4	1·495	1·478,	3·184	(100)*s	Biax (−)		1	12, 312, 368, 513,
(orthoboric		*b*	7·063(1)			1·48	6·08	(61)	α 1·331–1·340	X to base		527, 639, 731,
acid)	$P\bar{1}$	*c*	6·585(1)				5·94	(31)	β 1·448–1·457	88–90°		797
		α	92° 32(1)′				2·237	(17)	γ 1·453–1·459			
		β	101° 12(1)′				2·956	(16)	2V 5–17°			
		γ	119° 52(8)′				2·922	(16)	colourless			
		V	274·64(6)									
Metaborite	Cubic	*a*	8·886(1)	24	2·489	2·47,	4·442	(100)*s	Isotropic		5	425, 531, 727, 795
(metaboric						2·487	1·939	(93)	*n* 1·616–1·619			
acid)		V	701·65				3·627	(50)	colourless			
							6·28	(47)				
							3·973	(43)				
							2·809	(42)				
Borates												
Kernite	Monoc	*a* 7·016(1)	7·022	4	1·905	1·906(3)	7·40	(100)*n	Biax (−)	X ∧ *c*+38½°	3	318, 581, 777, 794
		b 9·152(2)	9·151(2)				6·64	(85)	α 1·454(1)	Y ∧ *c*−51½°		
	$P2_1/c$	*c* 15·678(2)	15·676				3·253	(34)	β 1·473(1)	Z=*b*		

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hardness	References
		Natural	Synthetic		(Calc.) $(g\,cm^{-3})$	(Meas.)	d (Å)	I				
							3·132	(29)	γ 1·488(1)	r > v, slight		
		β 108° 53(7)	108° 50(5)′				2·882	(29)	2V 80°			
							2·472	(27)	colourless			
		V 952·6(2)	953·4									
Tincalconite	Rhomb.	a	11·137(1)	9	1·912	1·880	2·926	(100)*s	Uniax (+)		2½	524, 600, 789, 797
		c	21·192(2)				4·392	(85)	ω 1·461			
	$R32$						3·452	(55)	ε 1·474			
		V	2276·4(2)				2·188	(38)	colourless			
							4·706	(31)				
							2·193	(30)				
Borax	Monoc	a 11·882(1)	11·8790(2)	4	1·713	1·715(5)	4·87	(100)*n	Biax (−)	X = b	2–2½	266, 487, 527, 797
		b 10·651(1)	10·6440(2)				2·564	(96)	α 1·4466	Z ∧ c−		
	$C2/c$	c 12·212(2)	12·2012(2)				5·70	(82)	β 1·4687	55° 35′		
		β 106° 39(1)′	106° 37·02(6)′				2·832	(79)	γ 1·4717	r > v, strong		
							2·846	(58)	2V 39° 58′			
									(calc.)			
		V 1480·8(2)	1478·3				3·936	(48)	colourless			
Biringuccite	Monoc	a	20·753(1)	4	2·375	(?)	3·452	(100)*s	Biax (−)	Y = b	(?)	129, 797
		b	6·561(1)				10·37	(81)	α 1·496(2)	Z ∧ a 5°		
	$P2_1/a$	c	11·198(1)				2·586	(48)	β 1·539(2)			
		β	93° 52(1)′				5·18	(42)	γ 1·557(2)			
							3·032	(21)	2V 63°			
		V	1521·3(2)				3·043	(19)	colourless			
Nasinite	Ortho	a	12·015(2)	4	2·133	2·134	2·897	(100)*s	Biax (−)		(?)	129, 797, 814
		b	6·518(1)				6·00	(99)	α 1·494			
	$Pna2_1$	c	11·173(1)				2·998	(85)	β 1·512			
		β	90° 04(1)′				5·29	(64)	γ 1·524			
							5·583	(19)	2V 67°			
		V	875·00				4·084	(17)	colourless			
Ezcurrite	Tricl.	a 8·598(2)		1	2·049	2·053	6·936	(100)*n	Biax (−)		3–3½	316, 746
		b 9·570(2)					3·074	(38)	α 1·468(1)			

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
	$P\bar{1}$	c 6·576(2)					4·494	(29)	β 1·507(1)			
		α 102° 45(3)′					3·135	(19)	γ 1·529(1)			
		β 107° 30(3)′					2·780	(19)	2V 73½°	$r > v$		
		γ 71° 31(3)′					2·039	(10)	colourless			
		V 484·7										
Ameghinite	Monoc	a 18·454(5)		4	2·037	2·030(6)	3·064	(100)*n	Biax (−)	$X \wedge c$ 9°	2½	19, 815
		b 9·895(5)					3·147	(76)	α 1·429(2)	$Z = b$		
	$C2/c$	c 6·322(5)					2·548	(29)	β 1·528(1)			
		β 104° 20′					3·352	(17)	γ 1·538(1)			
							2·914	(17)	2V 33°	$r < v$, weak		
		V 1118·5					4·951	(13)	colourless			
Aristarainite	Monoc	a 18·869(2)		2	2·102	2·027(5)	7·74	(100)*n	Biax (−)	$X = b$	3½	810
		b 7·531(1)					2·579	(19)	α 1·484(1)	$Y \wedge c = 38°$		
	$P2_1/a$	c 7·810(1)					3·037	(13)	β 1·498(1)	$Z \wedge a = 46°$		
		β 98°48·3(5)′					3·869	(12)	γ 1·523(1)			
							5·40	(11)	2V 70°	$r > v$, weak		
		V 1099·8(2)					2·400	(10)				
Rivadavite	Monoc	a 22·230(3)		2	1·915	1·905(2)	14·2	(100)*n	Biax (+)	$Z \wedge a - 32°$	3½	492a, 785, 797
		b 8·013(1)					7·59	(100)	α 1·470(1)	$Y = b$		
	$P2_1/a$	c 15·888(2)					2·950	(66)	β 1·481(1)			
		β 116° 42(1)′					3·246	(64)	γ 1·497(1)			
							6·23	(51)	2V 80°	$r > v$		
		V 2528·4(4)					4·740	(51)	colourless			
Sborgite	Monoc	a	11·119(8)	8	1·711	1·713	4·60	(100) s	Biax (+)		3½	132, 431, 590, 766, 797
		b	16·474(14)				3·30	(77)	α 1·432(2)			
	$C2/c$	c	13·576(9)				3·20	(76)	β 1·438			
		β	112° 50(2)′				2·572	(39)	γ 1·488(3)			
							3·56	(38)	2V 35°	$r > v$, weak		
		V	2291·9				6·88	(36)	colourless			
Probertite	Monoc	a 13·421(2)		4	2·132	2·135, 2·141	9·09	(100)*n	Biax (+)		3½	143, 244, 363, 391, 400, 587, 600, 732, 797
		b 12·558(1)					2·925	(30)	α 1·514–1·517	$Y = b$		
	$P2_1/a$	c 6·591(2)					6·61	(28)	β 1·520–1·525	$Z \wedge c$ 12°		

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	*d* (Å)	*I*			
		β 100° 01(1)′ V 1093·9(2)					3·993 4·553 3·536	(25) (21) (18)	γ 1·543–1·544 2V 70–73° *r* > *v* colourless		
Ulexite	Tricl P$\bar{1}$	*a* 8·813(1) *b* 12·857(1) *c* 6·676(1) α 90° 11(1)′ β 109° 15(1)′ γ 105° 05(1)′ V 686·3(1)		2	1·961	1·955(1)	12·35 7·77 6·00 4·156 2·665 4·341	(100)*n (85) (80) (67) (47) (45)	Biax (+) α 1·490–1·493 β 1·505–1·507 γ 1·528–1·531 2V 70–73° colourless	2½	13, 143, 146, 492a, 797, 798
Braitschite	Hexag *P**** (?)	*a* 12·256(1) *c* 7·377(5) V 944·02(13)		(?)	2·837	2·903(2)	4·283 3·021 10·52 2·810 3·168 3·155	(100)*n (92) (54) (53) (45) (38)	Uniax (+) ω 1·646(2) ε 1·647(2) colourless to white	(?)	571
Santite	Ortho *Aba*2	*a* 11·10 *b* 11·18 *c* 9·08 V 1126·8	11·065(2) 11·171(1) 9·054(1) 1119·1	4	1·740	1·740	3·36 3·52 5·60 2·767 2·181 5·93	(100)*s (84) (71) (50) (21) (15)	Biax (+) X = *c* α 1·422(2) Y = *b* β 1·435(2) Z = *a* γ 1·480(2) 2V 70° (calc.) colourless	2½	142, 154, 463, 731
Larderellite	Monoc $P2_1/a$	*a* 11·642(2) *b* 7·625(1) *c* 9·446(1) β 96° 52(1)′ V 832·5(2)		4	1·884	1·905(4)	9·36 2·920 4·69 2·958 5·43 2·892	(100)*n (73) (59) (45) (40) (36)	Biax (+) X = *b* α 1·493(1) Z ∧ *a* 30° β 1·509(1) γ 1·561(1) 2V 58° *r* < *v* colourless	(?)	141, 142, 164, 452, 462, 599, 797
Ammonioborite	Monoc *C*2/*c*	*a* 25·27(5) *b* 9·65(3) *c* 11·56(3)		4	1·759	1·765(4)	3·16 3·09 5·70	(100)*s (100) (60)	Biax (+) Y = *b* α 1·470 Z ∧ *c* 7° β 1·487	(?)	142, 461, 599

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	*d* (Å)	*I*				
		β 94° 17(5)′					2·876	(60)	γ 1·540			
							3·01	(50)	2V 60°	*r* < *v*		
		V 2811·1					8·98	(40)	colourless			
Hambergite	Ortho	*a* 9·75–9·78	9·74	8	2·299–	2·28–	3·81	(100)*n	Biax (+)	X = *a*	7–7½	45, 63, 104, 417,
		b 12·20–12·40	12·24		2·366	2·372	3·13	(90)	α 1·543–1·560	Y = *b*		527, 616, 660,
	Pbca	*c* 4·43–4·47	4·43				3·16	(45)	β 1·580–1·591	Z = *c*		730, 776, 795
		(OH)–(F)					4·52	(35)	γ 1·617–1·631			
		V 526·8–542·1	528·1				2·400	(35)	(F)–(OH)	*r* > *v*, weak		
							2·212	(35)	2V 84–90°			
									colourless			
Berborite	Hexag	*a* 4·43(3)	4·432	1	2·044	2·200(3)	5·3	(100)*n	Uniax (−)		3	497, 609
		c 5·33(3)	5·340				3·11	(100)	ε 1·485(2)			
	*P*321						2·656	(100)	ω 1·580(1)			
		V 90·6	90·84				2·044	(100)				
							2·208	(80)	colourless			
							1·705	(40)				
Rhodizite	Cubic	*a* 7·317(1)–		1	3·585	3·44–	2·983	(100)*n	Isotropic		8½	63, 91, 183, 184,
		7·319(1)				3·45	2·440	(51)	*n* 1·693(1)			249, 671
	*P*4̄3*m*						3·274	(48)				
		V 391·7–392·1					2·111	(37)	colourless to			
									white			
							1·775	(25)				
							1·956	(22)				
Wightmanite	Monoc	*a* 13·46		4	2·703	2·59	10·70	(100)*n	Biax (−)		5½	242, 493
		b 3·10					9·07	(100)	α 1·585(3)			
	*I*2/*m*	*c* 18·17					3·03	(30)	β 1·603(3)			
		β 91° 36′					4·74	(20)	γ 1·604(3)			
							2·446	(20)	2V 33°	*r* < *v*, strong		
		V 757·9					2·35	(20)	colourless			
Kotoite	Ortho	*a* 5·398	5·398	2	3·085	3·04–	2·67	(100)*s	Biax (+)	X = *a*	6½	284, 541, 594, 702,
		b 8·426	8·420		(n)	3·10	2·23	(100)	α 1·649–1·652	Y = *b*		703, 795

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) ($g\,cm^{-3}$)	(Meas.)	d (Å)	I				
	Pnmn	c 4·510 V 205·1	4·505 204·8		3·090 (s)		2·18 1·73 1·67 1·51	(100) (100) (100) (100)	β 1·652–1·656 γ 1·672–1·674 2V 20–34° colourless	Z=c r>v		
Suanite	Monoc $P2_1/a$	a 12·31(1) b 3·120(5) c 9·205(10) β 104° 20(5)′ V 342·53		4	2·913	2·91, 2·92	2·557 2·010 2·823 1·916 4·47 1·562	(100)*n (60) (50) (30) (25) (21)	Biax (−) α 1·596–1·606 β 1·639–1·645 γ 1·670–1·680 2V 70–76° colourless	X=b Y to perf. cleavage 23° r>v, weak	5½	70, 490, 500, 621, 666, 702, 704
Szaibelyite	Monoc $P2_1/a$	a 12·582(2) b 10·411(1) c 3·147(1) β 95° 38(1)′ V 410·3(1)	12·535(10) 10·377(5) 3·116(5) 93° 50(10)′ 404·4	4	2·724 (n) 2·763 (s)	2·60–2·76	2·209 5·22 2·669 6·27 3·036 2·434	(100)*n (63) (57) (51) (49) (41)	Biax (−) α 1·559–1·585 β 1·643–1·646 (2 detns.) γ 1·623–1·666 2V 5–28° colourless to white	X ∧ c 7–8° r>v	3–3½	40, 88, 196, 203, 234, 269, 273, 285, 383, 414, 514, 538, 576, 737, 739, 759, 797
Pinnoite	Tetra $P4_2$	a c V	7·620(2) 8·192(1) 475·70(3)	4	2·289	2·29	5·39 2·311 3·146 3·809 2·251 1·905	(100)*s (62) (41) (34) (28) (27)	Uniax (+) ω 1·565 ε 1·575 colourless		3½–4	377, 527, 532, 647, 777, 797
Inderite	Monoc $P2_1/a$	a 12·02(3) b 13·12(4) c 6·84(2) β 104° 40′ V 1043·5		4	1·781	1·785(2)	5·05 3·357 5·72 6·61 2·662 2·559	(100)*n (68) (60) (44) (44) (44)	Biax (+) α 1·487–1·489 β 1·491–1·493 γ 1·504–1·507 2V 37–38° colourless	Z ∧ c 5–9°	2½	75, 232, 247, 310, 585, 797

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
Kurnakovite	Tricl $P\bar{1}$	a 8·344(1) b 10·591(2) c 6·446(1) α 98° 46(1)′ β 108° 55(1)′ γ 105° 40(1)′ V 500·6(1)		2	1·856	1·847–1·861	4·92 3·470 7·24 2·477 2·532 2·679	(100)*n (82) (77) (54) (51) (42)	Biax (−) α 1·489–1·491 β 1·510–1·511 γ 1·520–1·525 2V 80° colourless	$r > v$, weak	3	248, 271, 297, 311, 572, 723, 797
Preobrazhenskite	Ortho $Pbcn$	a 16·32 b 9·19 c 10·52 V 1577·8		4	2·462	2·445(4)	5·26 3·77 4·06 3·18 3·22 2·63	(100)*n (96) (77) (59) (57) (52)	Biax (+) α 1·570–1·571 β 1·570–1·575 γ 1·593–1·595 2V 0–25° colourless	X = a Y = c Z = b $r > v$	4–5½	351, 518, 586, 642, 669, 670, 720, 797
Halurgite	Monoc $P*/c$	a 13·25(4) b 7·60(3) c 13·20(4) β 92° 09(10)′ V 1328·3		4	2·246	2·14(s) 2·19(n)	13·12 3·27 3·77 2·154 2·062 5·12	(100) s (100) (90) (80) (60) (50)	Biax (+) α 1·532(2) β 1·545(2) γ 1·575(2) 2V 70° (calc.) colourless	X = b Y ≈ a Z ≈ c	2½–3	348, 350, 424, 505
Hungchaoite	Tricl $P*$	a 8·811(1) b 10·644(2) c 7·888(1) α 103° 23(1)′ β 108° 35(1)′ γ 97° 09(2)′ V 666·2(1)	8·800(1) 10·648(2) 7·895(2) 103° 23(1)′ 108° 34(1)′ 97° 09(1)′ 666·3(1)	2	1·703 (n, s)	1·706(5) (n)	4·093 4·077 2·911 6·71 3·354 7·13	(100)*s (95) (70) (59) (53) (52)	Biax (−) α 1·445(2) β 1·485(2) γ 1·490(2) 2V 15(2)° colourless	X ∧ a + 28° Y ∧ c − 66° Z ∧ b + 37° $r < v$, distinct	1–2	108, 123, 124, 797
Kaliborite	Monoc $C2/c$	a 18·53(3) b 8·43(2) c 14·665(7) β 100° 08(7)′ V 2255·0		4	2·110	2·116	7·22 6·22 3·104 2·488 3·837 3·770	(100)*n (100) (71) (71) (50) (50)	Biax (+) α 1·508 β 1·527 γ 1·549 2V 81° colourless	Y = b Z ∧ c 64½°	4–4½	157, 158, 489, 527, 777

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å) Natural	Cell parameters (Å) Synthetic	Z	Density (Calc.) (g cm^{-3})	Density (Meas.)	X-ray powder data d (Å)	X-ray powder data I	Optical properties		Hardness	References
Aksaite	Ortho	a 12·56(1)	12·540(6)	8	1·966	2·066	6·4	(100)*s	Biax (−)	X = a	2½	68, 136, 165, 348
		b 24·33(3)	24·327(11)		(n)	(n)	4·72	(50)	α 1·470–1·473	Y = c		415, 505
	$Pbca$	c 7·50(1)	7·480(3)		1·975	1·99(1)	3·19	(50)	β 1·502–1·508	Z = b		
					(s)	(s)	3·11	(50)	γ 1·525–1·528			
		V 2291·9	2281·8				6·3	(35)	2V 70–75°			
							3·59	(35)	colourless			
Mcallisterite	Rhomb	a 11·543(5)	11·549(2)	6	1·866	1·867(5)	8·72	(100)*s	Uniax (−)		2½	21, 125, 166, 605
		c 35·556(5)	35·567(8)			(n)	2·807	(50)	ε 1·4635(3)n			
	$R\bar{3}c$					1·868	3·351	(42)	ω 1·5070(3)n			
		V 4102·8	4108			(s)	5·78	(35)				
							4·062	(35)	ε 1·4638 s			
							3·261	(35)	ω 1·5070 s			
									colourless			
Hydroboracite	Monoc	a 11·762(1)		2	2·173	2·167	5·77	(100)*n	Biax (+)	Y = b	2	128, 527, 549, 584,
		b 6·6831(5)					3·320	(82)	α 1·519–1·523	X ∧ c 33°		601, 797
	$P2/c$	c 8·234(1)					6·68	(63)	β 1·534–1·537			
		β 102° 36(1)′					4·462	(28)	γ 1·569–1·572			
							1·913	(27)	2V 60–66°			
		V 631·6(1)					2·436	(21)	colourless			
Inderborite	Monoc	a 19·197(3)		4	1·934	1·928–	6·07	(100)*n	Biax (−)	X ∧ c 2½°	3½	278, 322, 350, 394,
		b 7·426(1)				1·934	6·34	(40)	α 1·483–1·485	Y = b		397, 646, 797
	$A2/a$	c 12·131(1)					3·284	(26)	β 1·512			
		β 90° 20(1)′					3·201	(26)	γ 1·529–1·530			
							3·009	(19)	2V 77°			
		V 1729·2(3)					4·509	(15)	colourless			
Kurchatovite	Ortho	a 11·02		4	3·115	3·02	2·78	(100) n	Biax (−)	X = b	4½	440, 625
		b 36·0					1·922	(90)	α 1·635(1)	Y = a		
	$P2_12_12_1$	c 5·517					2·67	(80)	β 1·681(1)	Z = c		
							1·232	(80)	γ 1·698(1)			
		V 2189					2·26	(70)	2V 66°	$r > v$, slight		
							2·01	(70)	colourless to			
									pale grey			

Table II.—(*continued*)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hard-ness	References
		Natural	Synthetic		(Calc.) $(g\,cm^{-3})$	(Meas.)	*d* (Å)	*I*			
Wardsmithite	Hexag	No data		(?)	—	1·88(2)	13·5	(100) n	Uniax (−)	2½	212
	(?)						12·3	(62)	ε 1·476(2)		
							6·15	(55)	ω 1·490(2)		
							3·358	(51)	colourless		
							4·721	(42)			
							2·744	(26)			
Sibirskite	Ortho	No data		(?)	—	—	2·93	(100) n	Biax (−)	(?)	687
	(?)						2·58	(100)	α 1·555		
							1·878	(60)	β 1·643		
							3·74	(40)	γ 1·658		
							2·20	(40)	2V 43°		
							2·05	(40)	colourless		
Olshanskyite	Monoc	No data		(?)	—	2·23	2·81	(100) n	Biax (−)	4	73
	(?)						3·05	(80)	α 1·557(2)		
	Tricl						7·61	(50)	β 1·568(calc.)		
	(?)						6·78	(50)	γ 1·570(2)		
							2·57	(40)	2V 54(2)° $r>v$, weak		
							2·02	(40)	colourless		
Calciborite	Ortho	*a* 8·38(1)	8·369(1)	8	2·880	2·88(n)	3·456	(100)*s	Biax (−) $X=b$	3½	438, 547, 598, 624, 728
		b 13·82(1)	13·816(1)		(n)		3·57	(40)	α 1·595 $Y=a$		
	Pccn	*c* 5·006(2)	5·007(1)		2·884		7·16	(30)	β 1·654 $Z=c$		
					(s)		2·661	(30)	γ 1·670		
		V 579·75	578·94				1·789	(30)	2V 54°		
							4·04	(20)	colourless		
Korzhinskite	(?)	No data		(?)	—	—	2·02	(100) n	Biax (+)	(?)	439
							3·11	(70)	α 1·642(1)		
							2·81	(70)	β 1·647(1)		
							1·905	(50)	γ 1·672(1)		
							1·757	(40)	2V 44°		
							2·70	(30)	colourless		
Uralborite	Monoc	*a* 6·92		8	2·584	2·60	7·68	(100)*n	Biax (+)	4	443, 623, 626
		b 12·35					3·00	(100)	α 1·604(1)		

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hardness	References
		Natural	Synthetic		(Calc.) ($g\,cm^{-3}$)	(Meas.)	d (Å)	I			
	$P2_1/n$	c 9·80 β 97° V 831·3					1·148 3·43 2·26 2·053	(90) (80) (80) (80)	β 1·609(1) γ 1·615(1) 2V 85° colourless (?) $r>v$, strong		
Vimsite	Monoc $C2/c$	a 10·02(2) b 9·71(2) c 4·440(5) β 92° V 431·7		4	2·488	2·54	3·48 2·222 3·72 2·61 1·881 6·90	(100)*n (80) (70) (70) (70) (60)	Biax (−) α 1·584–1·585 β —— γ 1·613–1·614 2V 24–28° colourless	4	444, 623, 627, 628
Nifontovite	Monoc $C2/c$	a 13·102(9) b 9·507(5) c 13·437(8) β 118° 26(2)′ V 1471·8		4	2·352	2·36	7·28 3·84 2·238 2·063 2·75 2·214	(100)*n (80) (80) (80) (70) (70)	Biax (+) α 1·575(1) β 1·578(1) γ 1·584(1) 2V 76° colourless $r>v$, strong	3½	441, 623, 787
Frolovite	Tricl $P1$ (?)	a 7·80 b 5·70 c 7·95 α 71° 30′ β 101° 30′ γ 72° V 301·0	5·71 7·78 7·84 66° 74° 77° 303·3	2	2·182 (n) 2·165 (s)	2·14 n	6·17 3·840 3·478 2·516 2·340 3·622	(100)*s (90) (80) (80) (80) (70)	Biax (+) α 1·569–1·570 β 1·572 γ 1·580–1·582 2V 75° colourless	3½	423, 443, 548, 623, 698, 733
Pentahydroborite	Tricl $P\bar{1}$	a 7·875(2) b 6·534(2) c 8·104(2) α 111° 32′ β 111° 20′ γ 72° 42′ V 353·82		2	2·025	2·00–2·03	7·04 2·99 3·54 1·937 2·88 1·815	(100) n (90) (80) (80) (60) (60)	Biax (+) α 1·532(1) β 1·534(1) γ 1·542(1) 2V 74° colourless	2½	423, 443, 623, 817
Tyretskite	Tricl	a 6·44(2) b 6·45(2)		1	2·560	2·55	2·83 2·879	(100) n (90)	Biax (+) α′ 1·637	(?)	325, 348, 354

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	*d* (Å)	*I*				
	*P**	*c* 6·41(2) α 61° 46(3)′ β 60° 15(6)′ γ 73° 30(8)′ V 203·2					3·184 2·118 2·033 5·68	(70) (70) (70) (60)	β —— γ′ 1·670 2V 46° colourless			
Priceite	Tricl (?)	No data		(?)	——	2·41–2·48	10·9 3·63 5·46 3·49 2·72 2·18	(100) n (100) (80) (70) (60) (50)	Biax (−) α 1·572–1·573 β 1·591–1·594 γ 1·597–1·598 2V 32–33° colourless		3–3½	16, 18, 243, 369, 409, 422
Tertschite	Monoc (?)	No data		(?)	——	——	15·3 10·47 2·772 7·67 2·930 3·073	(100) n (97) (21) (16) (15) (12)	Biax (?) α′ 1·502 β —— γ′ 1·517 2V (?) colourless		(?)	459, 797
Fabianite	Monoc $P2_1/a$	*a* 6·593(1) *b* 10·488(2) *c* 6·356(1) β 113° 23(1)′ V 404·0(1)	1181·6(2)	4	2·787	2·77(1)	3·269 2·920 3·032 2·025 3·962 2·074	(100)*n (87) (83) (56) (54) (54)	Biax (−) α 1·612(2) β 1·636(2) γ 1·653(2) 2V 67(2)° colourless	X ∧ *a*+ 22(2)° Y = *b* Z ∧ *c*− 45(2)° *r* < *v*, very weak	6	210, 357
Colemanite	Monoc $P2_1/a$	*a* 8·728(1) *b* 11·254(1) *c* 6·0981(3) β 110° 07·2(3)′ V 562·43(3)		4	2·427	2·42–2·43	3·13 5·64 3·85 2·550 2·010 4·00	(100)*n (50) (50) (50) (50) (36)	Biax (+) α 1·58616 β 1·59216 γ 1·61409 2V 55° 52′ colourless	X = *b* Z ∧ *c* 82° 23′ *r* > *v*, very weak	4½	117, 118, 612, 613, 797
Meyerhofferite	Tricl $P\bar{1}$	*a* 6·637(1) *b* 8·343(1) *c* 6·481(1)		2	2·118	2·120	8·31 6·48 4·981	(100)*n (91) (25)	Biax (−) α 1·500(3) β 1·535(3)		2	120, 408, 602, 797

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
		α 90° 45·6(4)′ β 101° 59·2(6)′ γ 86° 43·7(4)′ V 350·5(4)					4·163 2·503 3·155	(23) (20) (18)	γ 1·560(3) 2V 79(5)° colourless	r > v, perceptible		
Inyoite	Monoc P2$_1$/a	a 10·621(1) b 12·066(1) c 8·408(1) β 114° 01(1)′ V 984·3(1)	10·63(2) 12·06(2) 8·405(20) 114° 02(5)′	4	1·873	1·874–1·875	7·67 2·526 3·368 1·968 2·547 3·450	(100)*n (25) (22) (22) (21) (20)	Biax (−) α 1·490–1·493 β 1·505–1·508 γ 1·516–1·521 2V 70–86° colourless	X ∧ c 37° Y = b	2	20, 140, 542
Volkovskite	Monoc P2$_1$	a 6·57(1) b 48·30(8) c 6·51(2) β 119° 05′ V 1805·4		8	2·347	2·295–2·34	8·1 3·28 2·63 2·81 2·15 1·980	(100)*n (90) (80) (70) (70) (70)	Biax (+) α 1·536(2) β 1·539(2) γ 1·603(2) 2V 24° (calc.) colourless	Y = b Z ∧ a 31°	(?)	355
Nobleite	Monoc P2$_1$/a	a 14·56(5) b 8·016(20) c 9·838(20) β 111° 45(10)′ V 1066·5	14·586(3) 8·019(1) 9·839(1) 111° 39(1)′ 1069·7(2)	4	2·098 (n) 2·092 (s)	2·09(1) (n) 2·10(1) (s)	6·78 2·096 3·451 5·18 2·849 2·565	(100)*s (36) (31) (30) (21) (21)	Biax (+) α 1·500(3) β 1·520(2) γ 1·554(2) 2V 76° (calc.) colourless	X ∧ a 29° Y = b Z ∧ c − 7° r > v, very weak	3	208, 797
Gowerite	Monoc P2$_1$/a	a 12·882(4) b 16·360(7) c 6·558(4) β 121° 37(3)′ V 1176·9	12·897(2) 16·353(5) 6·571(1) 121°29·7(7)′ 1181·6(2)	4	2·003 (n) 1·995 (s)	2·00(1)	8·19 3·183 4·089 2·728 9·15 2·646	(100)*s (27) (20) (19) (14) (11)	Biax (+) α 1·484(2) β 1·501(2) γ 1·550(2) 2V 61° colourless	Y = b X ∧ c 27°	3	207, 358, 797
Ginorite	Monoc P2$_1$/a	a 12·74(1) b 14·36(2) c 12·82(2) β 100° 46′	12·758(1) 14·314(2) 12·804(3) 101° 06(1)′	4	2·144 (n) 2·152 (s)	2·07–2·09 (n)	7·17 3·578 3·274 5·37	(100)*s (20) (17) (16)	Biax (+) α 1·517–1·526 β 1·521-— γ 1·577–1·580	Y = b	3½	12, 163, 303, 348, 349, 797

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
							2·083 3·532	(13) (8)	2V 42° colourless			
Kurgantaite	Tricl (?)	V 2304·1 No data	2297·7(5)	(?)	——	2·8–2·9	2·900 2·822 3·192 2·789 2·149 3·118	(100) n (100) (90) (70) (70) (60)	Biax (+) α 1·641 β 1·645 γ 1·672 2V small colourless		5–7	348, 354, 719
Unnamed mineral (Ca,Sr borate)	(?)	No data		(?)	——	——	2·821 1·988 1·260 3·13 1·624 1·150	(100) n (90) (70) (60) (60) (60)	Biax (+) α 1·642 β — γ 1·670 2V (?) colourless to white		(?)	693
Strontioborite	Monoc $P2_1$	a 9·83(3) b 8·22(2) c 7·55(2) β 107° 46(10)′		(?)	(?)	2·806	7·2 4·09 3·29 5·40 3·52 3·07	(100)*n (90) (80) (70) (70) (70)	Biax (+) α 1·470(2) β 1·510(2) γ 1·579(2) 2V 85° colourless		(?)	352, 426, 427
Strontioginorite	Monoc $P2_1/a$	V 581·0 a 12·856(1) b 14·460(1) c 12·794(2) β 101° 24(1)′		4	2·254	2·25–2·26	7·22 3·613 3·302 2·310 5·40 2·039	(100)*n (18) (9) (4) (3) (3)	Biax (+) α 1·512–1·513 β 1·524 γ 1·577–1·580 2V 44–52° colourless	Y=b	2–3	81, 360, 498, 499, 797
Veatchite	Monoc Aa	V 2331·6(3) a 20·860(5) b 11·738(3) c 6·652(2) β 92° 06′		4	2·665	2·66	10·5 3·32 2·600 3·47 2·865	(100)*n (35) (25) (20) (9)	Biax (+) α 1·543(2) β 1·553(2) γ 1·620(2) 2V 44(1)°	X ∧ c −30° Y ∧ a −28° Z=b r>v, weak	2	148, 150, 369, 661, 797

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
		V 1627·67(5)					5·64	(6)	colourless			
p-Veatchite	Monoc	a 6·729(20)		2	2·723	2·60–	10·4	(100)*n	Biax (+)	Y = b	(?)	47, 83, 147, 257,
		b 20·70(4)				2·685	3·31	(60)	α 1·551(2)			588, 651
	$P2_1$	c 6·581(20)					2·592	(30)	β 1·553(2)			
		β 119° 40(5)′					5·64	(20)	γ 1·621(2)			
							3·46	(20)	2V 37°			
		V 796·5					3·38	(15)	colourless			
Tunellite	Monoc	a 14·37(2)	14·390(3)	4	2·385	2·40(1)	6·57	(100)*s	Biax (+)	X ∧ a 29°	2½	52, 144, 209
		b 8·206(4)	8·213(2)		(n)	(n)	5·14	(32)	α 1·519(3)	Y = b		
	$P2_1/a$	c 9·93(1)	9·934(2)		2·382		6·97	(24)	β 1·534(2)	Z ∧ c − 5°		
		β 113° 53(6)′	114° 02(1)′		(s)		3·867	(21)	γ 1·569(2)			
							3·046	(19)	2V 68° (calc.)	$r > v$, weak		
		V 1070·7	1072·3				2·120	(19)	colourless			
Johachidolite	Ortho	a 7·968(1)		4	3·437	3·37(1)	2·632	(100)*n	Biax (+)	X = a	7½	767, 797
		b 11·724(1)					1·964	(49)	α 1·712(1)	Y = c		
	$Cmma$	c 4·374(1)					1·820	(27)	β 1·717(1)	Z = b		
							2·434	(25)	γ 1·726(1)			
		V 408·68(5)					2·001	(25)	2V 70(2)°	$r > v$,		
							1·754	(21)	colourless	strong		
Sinhalite	Ortho	a 9·878(1)		4	3·452	3·47–	2·14	(100)*n	Biax (−)	X = b	6½	135, 225, 534, 606,
		b 5·675(1)				3·504	1·621	(90)	α 1·667–1·676	Y = c		620, 736
	$Pnma$	c 4·328(1)					3·24	(70)	β 1·697–1·704	Z = a		
							2·62	(70)	γ 1·705–1·712			
		V 242·62					4·93	(60)	2V 51–56°			
							2·38	(60)	X deep brown			
									Y green			
									Z light brown	X > Y > Z		
Jeremejevite	Hexag	a 8·555(2)	8·590(5)	1	3·243	3·28	4·29	(100)*s	Uniax (−)		6½	122, 275, 276, 527,
		c 8·19(10)	8·220(5)		(n)	(n)	3·80	(100)	Anom. biaxial			747
	$P6_3/m$				3·205		2·81	(100)	ε 1·640(n)			
		V 519·1	525·3		(s)		2·21	(100)	ω 1·653(n)			
							2·062	(100)	ε 1·629(s)			

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I			
							2·66	(80)	ω 1·643(s) colourless		
Pinakiolite	Monoc $C*/*$	a 21·744(3) b 5·994(1) c 5·333(1) β 97° 38(1)′ V 691·72(15)		8	4·026	3·965	2·705 5·40 2·163 2·508 1·987 3·606	(100)*n (86) (20) (19) (6) (4)	Biax (−) α 1·908(5) β 2·05(1) γ 2·065(10) 2V 32(1)° $r<v$(?), moderate X deep reddish-brown Y nearly opaque Z reddish-brown Y>X>Z	6	408, 527, 797
Orthopinakiolite	Ortho $Pnn*$	a 18·45(3) b 12·70(2) c 6·07(1) V 1422·3		16	3·916	4·03(5)	2·59 5·17 2·52 2·03 2·20 1·523	(100)*n (90) (90) (90) (80) (80)	No data	(?)	570
Wiserite	Tetra (?)	a 14·30(1) c 3·32(1) V 678·9		4	3·810	3·42	14·2 2·53 6·40 3·36 2·87 2·35	(100)*n (80) (60) (60) (60) (60)	Uniax (−) Anom. biaxial ε 1·700–1·717 ω 1·753–1·76 E bright to dark orange O colourless to bright orange E>O	(?)	206
Jimboite	Ortho	a 5·638(5)		2	4·120	3·98	2·79	(100)*s	Biax (+) X=a	5½	593, 701

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
	Pnmn	b 8·714(3) c 4·633(7) V 227·62					1·801 2·33 1·732 4·11 3·62	(60) (50) (50) (40) (40)	α 1·792 β 1·794 γ 1·821 2V 35° colourless	$Y=b$ $Z=c$ $r>v$		
Sussexite	Monoc $P2_1/a$	a 12·832(2) b 10·700(1) c 3·283(1) β 94° 43(4)′ V 449·3(1)	12·738(5) 10·67(1) 3·272(5) 93° 00(10)′	4	3·393 (n) 3·432 (s)	3·0–3·31 (n)	6·32 2·744 2·478 1·788 3·43 3·32	(100)*n (80) (80) (60) (40) (40)	Biax (−) α 1·634–1·670 β 1·697–1·734 γ 1·704–1·738 2V —— X yellow-orange Z light orange to colourless $X>Z$		3½–5	88, 206, 250, 528, 554, 635, 743, 777, 797, 798
Roweite	Ortho *Pbam*	a 9·057(1) b 13·357(2) c 8·289(1) V 1002·8(1)		4	2·963 (Mn–end)	2·935(5)	3·974 2·600 2·184 2·264 1·708 1·641	(100)*n (72) (49) (32) (32) (29)	Biax (−) α 1·631–1·646 β 1·640–1·658 γ 1·641–1·660 2V 20–28° X very pale brown Y pale amber Z yellowish-brown	$X=c$ $Y=b$ $Z=a$ $r<v$, strong $Z>Y>X$	4½	442, 792, 793
Unnamed mineral ('Mineral X')	Monoc (?) (?)	a 11·57 b 3·4(3) c 8·20 β 109° 30′ V 304·1		(?)	——	——	10·77 5·41 3·69 2·94 1·795 7·68	(100) n (80) (80) (80) (80) (40)	Biax (?) α 1·690–1·710 β —— γ 1·76(approx.) 2V —— colour (?)		(?)	206

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) ($g\,cm^{-3}$)	(Meas.)	*d* (Å)	*I*				
Warwickite	Ortho *Pnam* (?)	*a* 9·20(1) *b* 9·45(1) *c* 3·01(1) V 261·7		2	3·432	3·3–3·35	2·59 2·97 6·66 2·10 1·994 4·21	(100)*n (30) (25) (25) (25) (20)	Biax (+) α 1·772–1·808 β (?)–1·813 γ 1·792–1·830 2V 55–59° X dark brown Y light to reddish-brown Z light brown	X = *c* Y = *b* Z = *a* X > Y > Z	4	6, 408, 449, 622, 668, 705, 795
Ludwigite	Ortho *Pbam*	*a* 9·19–9·37 *b* 12·17–12·36 *c* 2·99–3·07 V 334·4–350·3		4	3·702 (Mg-end)	3·62–4·41	5·12 2·547 2·515 2·027 2·167 2·990	(100)*n (70) (70) (50) (35) (25)	Biax (+) α 1·805–1·85 β ≈1·805–1·85 γ 1·915–2·15 2V 0–45° X bluish to dark green Y dark green to opaque Z dark brown to opaque	X = *a* Y = *b* Z = *c* *r* ≪ *v* Y > Z > X	6–7½	6, 26, 61, 87, 101, 228, 231, 334, 340, 373, 406, 408, 418, 419, 479, 480, 505, 529, 543, 603, 604
Azoproite	Ortho *Pbam*(?)	*a* 9·26(1) *b* 12·25(1) *c* 3·01(1) V 341·4		4(?)	—	3·63(2)	2·52 5·07 2·16 2·02 2·77 2·11	(100)*n (80) (60) (60) (50) (50)	Biax (+) α 1·799(20) β 1·822(30) γ 1·855(50) 2V 80° X light green Y dark green Z brownish-red	X = *b* Y = *a* Z = *c* Y > Z > X	6½	356, 777
Vonsenite	Ortho *Pbam*	*a* 9·39–9·50 *b* 12·26–12·40 *c* 3·06–3·10 V 257·9–365·2		4	4·809 (Fe end)	4·57–4·808	2·580 5·16 2·372 2·167 2·074 1·937	(100)*n (50) (25) (25) (18) (18)	opaque black		5–6	6, 61, 87, 197, 228–230, 373, 420, 480, 505, 667, 780

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I			
Hulsite	Monoc P*	a 10·684(3) b 3·099(1) c 5·438(2) β 94° 09(2)′ V 179·56(7)		2	——	4·5–4·6	2·664 5·35 2·585 2·039 4·99 2·491	(100)*n (70) (70) (50) (35) (35)	Biax (?) α 1·944–1·976 β —— γ 2·21–2·26 2V —— black with tinge of green, brown, or red	3	139, 178, 344
Bonaccordite	Ortho $Pbam$	a 9·213(6) b 12·229(7) c 3·001(2) V 338·11		4	5·187		2·548 2·514 5·10 1·898 4·61 2·334	(100)*n (100) (50) (50) (40) (35)	Biax*(?)	7	816
Nordenskiöldine	Rhomb $R\bar{3}$	a 4·860(1) c 15·950(1) V 326·3	4·859(2) 16·124(5) 329·7	3	4·219 (n) 4·176 (s)	4·12–4·20	2·906 3·735 1·799 5·38 2·203 4·093	(100)*s (80) (80) (40) (40) (20)	Uniax (−) ε 1·660 ω 1·778; 1·774(2)(s) colourless to yellow	5½–6	10, 179, 201, 453, 505
Behierite	Tetra $I4_1/amd$	a 6·206(5) c 5·472(5) V 210·8	6·213(2) 5·483(2) 211·64(1)	4	8·026 (Ta end)	7·86(5)	4·112 3·107 2·325 1·597 2·479 1·937	(100)*s (91) (39) (29) (28) (21)	Uniax (+) $\omega > 2·0$ $\varepsilon > 2·0$ Calc. mean index 2·12 colourless	7–7½	488, 797
Borates with Halogens											
Teepleite	Tetra $P4/nmm$	a c V	7·26(1) 4·85(1) 255·6	2	2·082	2·076	2·697 2·015 2·90 1·659 2·264 1·815	(100)*s (90) (80) (80) (70) (70)	Uniax (−) ε 1·503 ω 1·521 colourless	3–3½	241, 256, 582

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I			
Bandylite	Tetra $P4/n$	a 6·14 c 5·55 V 209·2		2	2·823	2·810	5·59 3·08 2·54 1·952 4·35 1·655	(100)*n (80) (80) (70) (60) (60)	Uniax (−) ε 1·641 ω 1·691 E pale greenish-yellow O deep cendre blue O > E	2½	153, 240, 525, 582
Satimolite	Ortho (?)	a 12·62 b 18·64 c 6·97 V 1639·6		2	1·698	1·70	3·20 9·5 6·3 4·01 3·51 2·441	(100)*n (90) (90) (90) (80) (80)	Biax (−) α 1·535(2) β 1·552(2) γ 1·552(2) 2V very small colourless	(?)	72, 517
Ivanovite	Monoc P*	a 8·62 b 8·04 c 14·75 β 91° 19′ V 1022		(?)	—	—	No data		Biax (−) α 1·504 β 1·523 γ 1·531 2V 58–72° $r < v$ colourless (?)	(?)	347, 498
Fluoborite	Hexag $P6_3/m$	a 9·06(2) c 3·06(1) V 217·5 (70% OH member)	8·805(6) 3·097(1) 207·94 (synth. F end)	2	2·790 (OH end) 3·014 (F end)	2·89–3·0	4·41 2·41 2·12 2·55 7·63 1·467	(100)*s (95) (90) (75) (65) (55)	Uniax (−) ε 1·482–1·534 ω 1·503–1·570 (F)–(OH) colourless	3½(?)	46, 85, 86, 111, 198, 215, 237, 238, 261, 262, 279, 283, 287, 331, 333, 421, 528, 540, 607, 614, 618, 654, 665, 682, 702, 795
Boracite	Ortho $Pca2_1$	a 8·5496 b 8·5496 c 12·0910(9)	8·54169 8·55049 12·09774	4	2·946	2·89–2·97	2·058 3·044 2·720 1·238	(100)*n (70) (50) (50)	Biax (+) X = c α 1·656–1·662 Y = a β 1·662–1·667 Z = b γ 1·668–1·673	7	286, 288, 295, 379, 559, 768, 786, 790, 795

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
		V 883·81	883·566				1·763	(45)	2V 82–82°			
							1·357	(40)	colourless to			
									green			
Ericaite	Ortho	a 8·608(2)		4	3·571	3·17–	No data		Biax (?)		7(?)	173, 379, 714, 786
	(?)	b 8·608(2)			(Fe	3·503			No data			
	$Pca2_1$	c 12·165(3)			end)				Raspberry red			
	(?)	V 901·4										
Congolite	Rhomb	a 8·612(2)	8·6240	6	3·576	3·567–	2·725	(100)*n	Uniax (−)		7½(s)	379, 610, 714, 744,
		c 21·065(4)	21·0489		(Fe	3·58	3·05	(80)	ε 1·731(2)			786
	$R3c$				end)	(s)	2·061	(75)	ω 1·755(5)			
		V 1353·0	1355·7				2·058	(75)	pale red			
							1·838	(70)				
							1·834	(70)				
Chambersite	Ortho	a 8·68(1)	8·683(2)	4	3·468	3·477–	3·07	(100)*n	Biax (+)		7	66, 295, 307, 738,
		b 8·68(1)	8·689(2)		(Mn	3·49	2·74	(60)	α 1·732(1)			762, 768
	$Pca2_1$	c 12·26(1)	12·284(2)		end)		2·08	(60)	β 1·737(1)			
							3·54	(50)	γ 1·744(1)			
		V 923·7	926·78				2·17	(50)	2V 83(3)°			
							1·851	(50)	colourless to			
									purple			
Chelkarite	Ortho	a 13·69		(?)	——	——	3·53	(100)*n	Biax (+)		(?)	23, 348, 781
		b 20·84					10·42	(90)	α 1·520			
	$Pbca$	c 8·26					2·209	(80)	β ——			
							4·96	(70)	γ 1·559			
		V 2356·6					2·029	(70)	2V (?)			
							6·68	(50)	colourless			
Hydrochlorborite	Monoc	a 22·783(3)		4	1·876	1·852(5)	8·48	(100)*n	Biax (+)		2½	112, 113, 812
		b 8·745(1)					6·01	(24)	α 1·499, 1·501	X ∧ c 25°		
	$I2/a$	c 17·066(1)					3·604	(9)	β 1·502, 1·504	Y = b		
		β 96° 42·3(4)					2·798	(8)	γ 1·521, 1·520			
							2·825	(7)	2V 45°, 46°			
		V 337 6·9(3)					2·186	(7)	colourless	$r<v$		

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm⁻³)	(Meas.)	d (Å)	I			
Hilgardite	Monoc *Cc*	*a* 6·31(2) *b* 11·33(1) *c* 11·44(1) β 90° V 817·9		4	2·693	2·71	2·85 2·11 1·99 2·755 2·546 1·873	(100)*n (80) (80) (60) (60) (60)	Biax (+) X∧*c* 88½ α 1·630(2) Y=*b* β 1·636(2) Z∧*c* 1½ γ 1·664(2) 2V 35° r>*v* colourless	5	82, 317, 642, 795
Parahilgardite	Tricl *P*1	*a* 6·31(2) *b* 6·484(4) *c* 17·50(2) α 84° 00′ β 79° 36′ γ 60° 54′ V 615·2		3	2·686	2·71	2·87 2·83 2·755 2·125 2·033 5·70	(100)*n (100) (80) (80) (80) (60)	Biax (+) α 1·630 β 1·636 γ 1·664 2V 35° *r*>*v* colourless	5	82, 319, 795
Strontio-hilgardite	Tricl *P*1	*a* 6·479(5) *b* 6·608(5) *c* 6·380(20) α 118° 48′ β 119° 29′ γ 77° 09′ V 208·32		1	3·022	2·993	2·89 2·82 2·775 2·142 2·137 2·053	(100)*n (100) (100) (80) (80) (80)	Biax (+) α 1·633–1·638 β ——–1·639 γ 1·666–1·670 2V 19(3)° colourless	5–7	82, 186, 354, 385
Solongoite	Monoc *P*2₁/*a*	*a* 12·54(2) *b* 7·26(1) *c* 7·93(1) β 94°0(15)′ V 720·2		2	2·493	2·514	2·196 7·84 1·734 2·61 2·54 1·911	(100)*n (90) (90) (80) (80) (80)	Biax (+) Z∧*c*=25° α 1·510(1) β 1·510(1) γ 1·545(1) 2V very small *r*>*v*, very weak	3½	811
Aldzhanite	Ortho *Pbca*	*a* 12·76 *b* 14·59 *c* 8·19 V 1524·7		4	——	2·21	7·46 2·987 2·548 3·49 2·503 2·171	(100)*n (90) (90) (80) (80) (80)	Biax (+) α 1·600 β —— γ 1·620 2V (?) colourless to pale pink	(?)	23, 348, 781

Table II.— (continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
Borates with Carbonate												
Sakhaite	Cubic	a 14·6062(7)		1	2·808	2·78–	2·58	(100)*n	Isotropic		5	516, 519, 797
						2·83	2·108	(56)	n 1·639–1·646			
	F***	V 3116·1(4)					5·16	(22)	colourless			
							1·827	(21)				
							1·951	(14)				
							2·81	(13)				
Carboborite	Monoc	a 11·433(2)		2	2·091	2·12	5·72	(100)*n	Biax (−)	Y = b	2	309, 797
		b 6·700(2)					4·345	(27)	α 1·507(1)			
	$P2_1/a$	c 10·720(3)					2·757	(22)	β 1·546(1)			
		β 120° 19(1)′					3·278	(18)	γ 1·569(1)			
							3·209	(17)	2V 75°			
		V 708·8(2)					3·133	(16)	colourless			
Borcarite	Monoc	a 17·81(2)		2	2·791	2·77(1)	2·660	(100)*n	Biax (−)	Y ∧ c 28(4)°	5	539, 644, 777
		b 8·36(1)					1·881	(90)	α 1·590–1·594	Z = b		
	$C2/m$	c 4·46(1)					2·904	(80)	β 1·651–1·653			
		β 102° 0′					2·723	(70)	γ 1·657–1·660			
							2·263	(60)	2V 30(2)°			
		V 649·5					1·695	(60)	colourless			
Gaudefroyite	Hexag	a 10·66(5)		2	3·504	3·50(2)	2·95	(100)*n	Uniax (+)		6-6½	280, 332, 777
		c 5·87(2)				(3·44-	2·62	(100)	ω 1·81(1)			
	$P6_3/m$					'corrected')	2·46	(100)	ε 2·02(1)			
		V 577·7					9·1	(80)	E red-orange			
							4·54	(80)	O light russet	E > O		
							2·69	(80)				
Borates with Phosphate or Arsenate												
Cahnite	Tetra	a 7·0952(15)		2	3·175	3·06–	3·56	(100)*n	Uniax (+)		3	94, 204, 437, 527, 567
		c 6·1904(3)				3·156	1·818	(52)	ω 1·655–1·662			
	$I\bar{4}$						2·640	(48)	ε 1·656–1·663			
		V 311·64					5·02	(20)	colourless			
							4·67	(20)				
							2·833	(19)				

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
Teruggite	Monoc	a 15·675(13)		2	2·193	2·149–	12·13	(100)*n	Biax (+)	$X \wedge c - 26°$	2½	22, 167
		b 19·920(14)				2·20	2·785	(30)	α 1·526(1)	$Z = b$		
	$P2_1/a$	c 6·255(4)					9·98	(22)	β 1·528(1)			
		β 99° 20(5)′					3·577	(22)	γ 1·551(1)			
							4·65	(21)	2V 33°	$r > v$, weak		
		V 1927·2					8·37	(20)	colourless			
Lüneburgite	Monoc	a 9·81		2	2·114	2·07–	4·95	(100) s	Biax (−)	$Y \wedge a - 32°$	1–2	80, 272, 408, 515,
		b 7·62				2·10	4·86	(82)	α 1·518–1·526	$Z = b$		683, 797
	A*	c 10·10					5·02	(78)	β 1·540–1·543			
		β 97° 24′					2·978	(50)	γ 1·544–1·549			
							2·824	(47)	2V 42–55°			
		V 748·7					3·240	(41)	colourless			
Seamanite	Ortho	a 7·811(5)		4	3·133	3·08–	6·92	(100)*n	Biax (−)	$X = a$	4	370, 398, 434, 485
		b 15·114(10)				3·128	2·842	(80)	α 1·640(3)	$Y = b$		
	$Pbnm$	c 6·691(5)					3·777	(70)	β 1·663(3)	$Z = c$		
							2·502	(70)	γ 1·665(3)			
		V 789·9					7·55	(60)	2V 40°	$r < v$		
							4·204	(60)	pale yellow			
Borates with Sulphate												
Heidornite	Monoc	a 18·774(5)		4	2·712	2·753(2)	3·120	(100)*n	Biax (+)	$Y = b$	4–5	96, 205, 797
		b 7·825(2)					2·753	(17)	α 1·580	$Z \wedge a$ 23°		
	$A2/a$	c 10·184(4)					3·788	(16)	β 1·588			
		β 93° 16(2)′					2·970	(14)	γ 1·604			
							2·546	(10)	2V 63–77°	$r < v$		
		V 1493·6(6)					1·988	(9)	colourless			
Sulfoborite	Ortho	a 10·132(1)		4	2·439	2·40–	3·11	(100)*n	Biax (−)	$X = a$	4–4½	80, 267, 348, 353,
		b 12·537(1)				2·44	5·58	(90)	α 1·522–1·529	$Y = b$		399, 408, 428,
	$Pnma$	c 7·7748(8)					2·063	(90)	β 1·540–1·541	$Z = c$		429, 650, 674,
							3·97	(80)	γ 1·551–1·554			797
		V 987·59					3·51	(80)	2V 70–88°			
							3·16	(80)	colourless to pink			

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	*d* (Å)	*I*				
Silicoborates												
Howlite	Monoc $P2_1/c$	*a* 12·78(3) *b* 9·33(2) *c* 8·60(2) β 104° 50(6)′ V 991·3(1)		4	2·622	2·56–2·607	6·20 4·13 12·38 3·10 2·477 2·064	(100)*n (75) (72) (60) (37) (31)	Biax (−) α 1·583–1·590 β 1·596–1·600 γ 1·605–1·607 2V 67–73° colourless	X=*b* Z∧*c* 50°	4	128, 235, 382, 408, 492, 692, 777
Garrelsite	Monoc $C2/c$	*a* 14·639(3) *b* 8·466(2) *c* 13·483(3) β 114° 13(1)′ V 1524·0		4	3·882	3·68	3·053 3·636 2·026 2·873 2·757 6·125	(100)*n (90) (80) (70) (70) (50)	Biax (−) α 1·620(3) β 1·633(3) γ 1·640(3) 2V 55(2)° colourless	X∧*c* 3½° Y=*b*	6	754, 800
Borosilicates												
Manandonite	Monoc (?)	*a* 5·23 *b* 8·92 *c* 14·11 β 97° 45′ V 652·2		2	2·530	2·89	No data		Biax (+) α —— β 1·6 γ —— 2E 25–30° colourless	Z near *c*	(?)	408, 653
Tourmaline (Group)												
Elbaite	Rhomb $R3m$	*a* 15·84–15·93 *c* 7·10–7·13 V 1542·8–1566·9	15·843(2) 7·102(2) 1543·8	3	3·015–3·068	3·00–3·11	2·560 2·878 3·961 3·438 1·776 2·805	(100)*s (84) (60) (50) (46) (44)	Uniax (−) ε 1·618–1·630 ω 1·635–1·651 O light blue, green, pink, red, colourless E colourless	O > E	7–7½	37, 43, 172, 202, 384, 402, 502, 579, 638, 677, 694, 716, 751
Dravite	Rhomb $R3m$	*a* 15·92–15·98 *c* 7·19–7·24	15·947(2) 7·194(2)	3	2·987–3·018 (Mg end)	2·98–3·15	2·576 3·99 2·961	(100)*n (85) (85)	Uniax (−) ε 1·608–1·636 ω 1·627–1·664		7–8	14, 28, 31, 38, 171, 172, 177, 187, 188, 251, 263,

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I			
		V 1582·1–1598·9	1584·4				4·22 3·48 2·040	(65) (60) (45)	E pale yellow to colourless O brown, light brown, yellow (to opaque) O≫E ε 1·638–1·642 (chromian dravite) ω 1·685–1·687 (chromian dravite) E yellow-green O blue-green O>E		342, 362, 467, 502, 535, 556, 557, 637, 638, 648, 657, 659, 663, 672, 677, 694, 697, 707, 716, 748, 761, 764, 804, 806
Schorl	Rhomb *R*3*m*	*a* 15·93–16·05 *c* 7·12–7·24 V 1564·7–1615·2	16·095(2) 7·136(2) 1600·9	3	3·354–3·430 (Fe end)	2·92–3·28	2·912 2·581 1·633 1·785 4·004 2·494	(100)* s (69) (69) (64) (56) (54)	Uniax (−) ε 1·627–1·662 ω 1·653–1·690 E pale yellow to colourless O brown, blue, green (to opaque) O≫E	7–8	39, 168, 172, 253, 384, 435, 502, 522, 556, 637, 638, 641, 657, 677, 694, 695, 716, 718, 764
Tsilaisite	Rhomb *R*3*m*	*a* *c* V	15·990(2) 7·137(2) 1580·3	3	3·312	3·09–3·135	2·578 3·975 2·905 2·946 3·453 3·464	(100)* s (93) (74) (62) (51) (44)	Uniax (−) ε 1·622–1·641 ω 1·643–1·659 E colourless O pale pink, brown, grey O>E	7–(?)	37, 155, 456, 636, 672, 677
Uvite	Rhomb	No data		3	—	3·075	2·564 1·272	(100) n (100)	Uniax (−) ε 1·636–1·646	7–(?)	180, 384, 672, 699

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
	*R*3*m*						2·945 1·019 3·449 2·031	(90) (90) (80) (80)	ω 1·662–1·678 E yellow, pale grey, colourless O brown, light brown, maroon, olive	O > E		
Buergerite	Rhomb *R*3*m*	*a* 15·8708(4) *c* 7·1919(4) V 1568·81(9)	15·860 7·173 1562·6	3	3·292	3·30–3·31	3·970 2·569 2·958 3·481 4·215 1·587	(100)*n (67) (44) (38) (33) (33)	Uniax (−) ε 1·655(3) ω 1·735(3) E very pale yellow O yellow-brown	O > E	7–8	42, 181, 182, 455, 797
Reedmergnerite	Tricl *C*$\bar{1}$	*a* 7·833(1) *b* 12·360(2) *c* 6·803(1) α 93° 18·5(7)′ β 116° 21·1(5)′ γ 92° 03·3(8)′ V 587·77(5)		4	2·780	2·70–2·776	3·874 3·078 3·038 2·841 3·137 3·651	(100)*n (79) (79) (48) (41) (40)	Biax (−) α 1·554–1·558 β 1·565–1·565 γ 1·572–1·573 2V 74–81° colourless		6–7	17, 190, 466
Searlesite	Monoc *P*2$_1$	*a* 7·970(1) *b* 7·058(1) *c* 4·8988(3) β 93° 57·1(4)′ V 274·9(3)		2	2·464	2·44–2·462	4·042 3·226 4·296 2·911 3·529 3·464	(100)*n (98) (61) (61) (60) (58)	Biax (−) α 1·515–1·523 β 1·531–1·533 γ 1·535–1·535 2V 74° colourless	X ∧ *c* 32–34° Z = *b*	3½	33, 224, 245, 578, 797
Datolite (Group) Datolite	Monoc	*a* 9·636(8) *b* 7·608(4)	9·64 7·62	4	2·999 (n)	2·966–3·02	3·114 2·857	(100)*s (95)	Biax (−) α 1·621–1·634	Y = *b* Z ∧ *a* 1–4°	5–6	15, 27, 62, 79, 110, 172, 189, 217,

Table II.—(*continued*)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
	$P2_1/a$	c 4·832(4)	4·82		3·001		2·986	(56)	β 1·649–1·658			265, 294, 371,
		β 90° 24(4)′	90° 00′		(s)		3·75	(55)	γ 1·664–1·674			468, 521, 530,
							2·245	(51)	2V 70–74°			550, 717, 725,
		V 354·24	354·1				2·189	(42)	colourless	$r>v$, weak		776, 788
'Mineral A'	Monoc	a 9·86		(?)	——	3·78	2·83	(100) n	Biax (−)		6	615
		b 7·48					3·09	(90)	α 1·720			
	$P2_1/a$(?)	c 4·66					2·54	(70)	β ——			
		β 91° 30′					2·19	(50)	γ 1·731			
							1·96	(40)	2V 75°			
		V 343·6					3·71	(30)	greenish-grey to colourless			
Bakerite	Monoc	a 9·60		4	2·944	2·885	3·11	(100)*n	Biax (−)	Y=b	4½	128, 369, 491
		b 7·60					2·85	(60)	α 1·624	Z ∧ a 44°		
	$P2_1/a$	c 4·82					2·236	(60)	β 1·635			
		β 90° 12′					3·74	(50)	γ 1·654			
							2·51	(50)	2V 87–88°			
		V 351·66					2·18	(50)	colourless			
Homilite	Monoc	a 9·67		4	3·577	3·34–3·38	3·10	(100)*n	Biax (+)	Y ∧ c near 0°	5	408, 652, 795, 796
		b 7·57					2·52	(100)	α 1·715(3)			
	$P2_1/a$	c 4·74					2·83	(90)	β 1·725(3)	Z=b		
		β 90° 22′					2·97	(70)	γ 1·738(3)			
							2·18	(70)	2V 80°	$r>v$, strong		
		V 347·0					2·23	(60)	X bluish-green			
									Y deep brownish-red			
									Z deep smoky grey to brownish-yellow			
Danburite	Ortho	a 8·01–8·05	8·03(1)	4	2·981–3·022	2·95–3·09	3·575	(100)*s	Biax (−) to (+)	X=a	7–7½	29, 109, 217, 291,
	Pnam	b 8·75–8·79	8·76(1)				2·967	(100)	α 1·627–1·632	Y=c		292, 293, 330,
		c 7·71–7·74	7·74(1)				2·747	(65)	β 1·630–1·637	Z=b		363, 381, 387,

Refs. p. 54

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hardness	References
		Natural	Synthetic		(Calc.) $(\mathrm{g\,cm^{-3}})$	(Meas.)	d (Å)	I			
		V 540·4–547·7	544·4				3·447 2·738 2·658	(60) (60) (52)	γ 1·633–1·644 2V 84–93° $r < v$, strong colourless to pale yellow		634, 715, 772, 773, 776, 799
Axinite (Group) Ferroaxinite	Tricl $P\bar{1}$	a 8·9585(22) b 9·1995(20) c 7·1566(15) α 102° 42(1)′ β 98° 08(1)′ γ 88° 15(1)′ V 569·6		2	3·324	3·19–3·35	2·812 3·16 3·46 6·30 3·68 3·28	(100) n (90) (80) (70) (60) (60)	Biax (−) α 1·659–1·690 β 1·665–1·698 γ 1·668–1·699 2V 64–80° $r < v$, weak to strong X colourless to pale pink, brown Y colourless to pink, violet Z colourless to light yellow Y > X > Z	6½–7¼	24, 32, 50, 76, 95, 102, 107, 172, 239, 258, 323, 324, 336, 374, 384, 400, 401, 412, 464, 477, 523, 596, 617, 640, 643, 658, 684, 696, 741, 769, 776, 779
Manganaxinite	Tricl $P\bar{1}$	a 8·978(3) b 9·190(3) c 7·161(3) α 102° 44(1)′ β 98° 12(2)′ γ 88° 16(2)′ V 570·3		2	3·314	3·20–3·34	No data		Biax (−) α 1·674–1·689 β 1·680–1·696 γ 1·683–1·700 2V 64–85° $r < v$, strong X colourless to pale brown Y colourless to violet Z colourless to light yellow Y > X > Z	6½–7 (?)	35, 246, 264, 400, 401, 509, 523, 536, 595, 596
Tinzenite	Tricl	a 8·874 b 9·129		2	3·509	3·26–3·39	2·812 3·46	(100) n (80)	Biax (−) α 1·687–1·693	6½–7 (?)	400, 401, 465, 523, 537, 573, 596

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Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hard-ness	References
		Natural	Synthetic		(Calc.) ($g\,cm^{-3}$)	(Meas.)	d (Å)	I			
	$P\bar{1}$(?)	c 7·095 α 103° 16′ β 98° 16′ γ 88° 39′ V 552·7					6·30 3·14 2·975 2·152	(70) (70) (70) (70)	β 1·693–1·701 γ 1·697–1·706 2V 63–89½° pale yellow to yellow-orange		
Harkerite	Cubic F***	a 29·496(2) V 25661(6)		8	2·944	2·94–2·959	2·61 2·124 5·22 1·510 3·00 3·39	(100)*n (22) (20) (17) (8) (7)	Isotropic; Anom. birefringence n 1·653(1) colourless	(?)	516, 519, 675, 797
Melanocerite	Hexag $P6_3/m$	a 9·41–9·52 c 6·88–6·99 V 527·6–548·6		(?)	—	3·42–4·45	2·81 1·940 1·835 1·754 3·08 2·70 (after heating to 900°C)	(100) n (70) (70) (60) (50) (50)	Isotropic to Uniax (−) n 1·65–1·77 light to deep reddish-brown, to black	5	388, 390, 408, 558, 591, 678, 784, 797, 799
Caryocerite	Hexag $P6_3/m$ (?)	a 9·35 c 6·88 V 520·9 (after heating to 900°C)		(?)	—	4·13–4·45	2·787 1·830 3·129 1·743 1·106 3·405 (after heating to 900°C	(100) n (90) (70) (60) (60) (50)	Isotropic to Uniax (−) n 1·697–1·76 nut brown	4½–6	378, 688, 783
Tritomite	Hexag	a 9·35 c 6·88		(?)	—	4·16–4·66	2·81 3·44 1·24	(100)*n (40) (40)	Isotropic (unheated) n 1·650–1·757	5½	329, 796

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I			
	$P6_3/m$	V 520·9 (after heating to 600–1000°C)					3·08 2·70 1·94 (after heating to 600–1000°C)	(30) (30) (30)	dark brown		
Spencite	Hexag $P6_3/m$	a 9·32 c 6·84 V 514·5 (after heating to 1000°C)		(?)	—	3·05–3·40	2·78 4·02 3·13 1·111 1·103 3·83 (after heating to 1000°C)	(100)*n (50) (50) (50) (50) (40)	Isotropic (unheated) n 1·627–1·670 pale brown to pale green	3½, 6½	252, 329
Stillwellite	Hexag $P3_1$	a 6·907 c 6·768 V 279·62 (unheated)	6·845 6·694 271·62 (Ce end)	3	4·603	4·57–4·70	2·921 4·447 3·431 2·970 1·867 2·129 (after heating to 1000°C)	(100)*n (90) (90) (80) (80) (70)	Uniax (+) Anom. biax. ω 1·765–1·784 ε 1·783–1·792 2V 0–6° colourless	6½	192, 193, 259, 432, 503, 690, 691
Hellandite	Monoc $P2/a$	a 18·824(4)–18·911(4) b 4·696(1)–4·708(1) c 10·248(2)–10·276(2) β 111° 26(1)′–111° 31(1)′ V 843·24–851·14		4	—	2·95–3·55	2·812 4·69 2·635 2·603 3·436 3·198	(100)*n (80) (80) (80) (70) (70)	Biax (−) α 1·652–1·72 β 1·657– —— γ 1·662–1·73 2V 48–87° colourless to pale yellow X=b Z ∧ c 6–44°	4½–6½	306
Tadzhikite	Tricl(?)	a 17·93		2	3·84	3·73	2·65	(100) n	Biax (−) to (+)	6	199

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I			
('Tadzhikite II')	(?)	*b* 4·71 *c* 10·39 α ≈90° β 100° 45′ γ ≈90° V 862					1·913 4·97 2·94 1·665 2·86	(55) (30) (30) (30) (25)	α 1·750 β —— γ 1·763 2V 80–92° brown		
Cappelenite	Hexag (?)	No data		(?)	——	4·407	2·78 3·46 1·94 4·62 3·27 2·30	(100) n (50) (50) (30) (20) (20)	Uniax (−) ε —— ω 1·76	6–6½	795, 796, 799
Painite	Hexag $P6_3$**	*a* 8·725(5) *c* 8·46(1) V 557·7		1	——	4·00(2)	5·76 2·520 3·70 2·370 2·008 1·726	(100)*n (100) (80) (80) (80) (60)	Uniax (−) ε 1·7875 ω 1·8159 E pale brownish-orange O ruby red O > *E*	≈8	134
Serendibite	Tricl *P**	*a* 8·630(3) *b* 9·826(3) *c* 10·393(3) α 103° 35(1)′ β 106° 22(1)′ γ 118° 13(1)′ V 670·79		2	3·519	3·42–3·515	3·35 2·85 2·59 2·47 2·03 1·425	(100) n (100) (100) (100) (100) (100)	Biax (+) α 1·701–1·738 β 1·703– —— γ 1·706–1·743 *r* < *v*, strong or *r* > *v*, strong 2V 80–90° X pale yellowish-green Y colourless to pale green Z dark blue to bluish-green	6½	408, 410, 544, 575, 622, 726, 750, 778, 799
Grandidierite	Ortho *Pbnm*	*a* 10·335(2) *b* 10·978(2) *c* 5·760(2)		4	3·088	2·91–2·99	5·17 5·04 5·48	(100)*n (100) (80)	Biax (−) X = *b* α 1·580–1·602 Y = *c* β 1·618–1·636 Z = *a*	7–7½	49, 67, 174, 345, 436, 649, 777

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hardness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	*d* (Å)	*I*				
		V 653·52					2·744 2·166 3·708	(80) (60) (50)	γ 1·620–1·638 2V 24–30° X pale blue to blue Y colourless Z pale greenish-blue to blue-green	$r<v$, strong or $r>v$, strong Z > X > Y		
Kornerupine	Ortho *Cmcm*	*a* 13·675–13·767 *b* 15·937–16·100 *c* 6·68–6·735 V 1455·8–1492·8	13·736(6) 16·147(10) 6·754(4) 1498·0 (boron-free)	4	—	3·24–3·449	2·613 3·006 3·345 2·096 10·36 1·674	(100)*n (78) (48) (37) (36) (25)	Biax (−) to pseudo-uniaxial (−) α 1·665–1·682 β 1·677–1·696 γ 1·677–1·710 2V 3–50° For Z > Y > X: X colourless to pale yellowish-brown, green Y colourless to pale green, yellow, pink Z pale to dark green, brownish-green For Y > Z > X:	X = *c* Y = *b* Z = *a* $r>v$, weak or $r<v$, weak	6–7	30, 41, 174, 270, 289, 304, 305, 346, 403, 436, 481, 484, 494, 608, 611, 678, 736, 797, 803

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties	Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I			
Dumortierite	Ortho *Pmcn*	a 11·71–12·2(2) b 20·19–21·4(1) c 4·69–4·72(1) V 1109–1232		4	—	3·21–3·48	2·549 5·89 5·84 5·09 2·926 3·227	(100)*n (90) (90) (90) (90) (85)	X pale brown Y dark green, bluish-green Z pale green, brown Biax (−) $X=c$ α 1·655–1·695 $Y=b$ β 1·675–1·722 $Z=a$ γ 1·683–1·723 $r<v$, strong 2V 10–51° or $r>v$, strong X deep blue, green, brown, to black; or pale tints of violet, red, yellow, etc. Y colourless to blue, orange, red-brown, etc. Z colourless to yellow, brown $X \gg Y > Z$	7–8½	48, 121, 133, 195, 233, 255, 339, 341, 411, 430, 446, 495, 510, 555, 569, 592, 631, 724, 735, 753, 795, 797, 801, 802, 805
Holtite	Ortho *Pmcn*	a 11·905(5) b 20·355(5) c 4·690(1) V 1136·5		4	—	3·90(2)	10·28 2·94 5·89 5·93 5·08	(100)*n (40) (34) (32) (32)	Biax (−) $X=c$ α 1·743–1·746 β 1·756–1·759 γ 1·758–1·761 2V 49–55° $r<v$	8½	568

Table II.—(continued)

Mineral	System and space group	Cell parameters (Å)		Z	Density		X-ray powder data		Optical properties		Hard-ness	References
		Natural	Synthetic		(Calc.) (g cm^{-3})	(Meas.)	d (Å)	I				
							5·12	(24)	X yellow Y colourless Z colourless			
Tienshanite	Hexag P***	a 16·755(10) c 10·435(7) V 2537·0		6	3·127	3·29	4·19 3·177 3·474 2·803 2·419 10·5	(100)*n (90) (80) (50) (50) (35)	Uniax (−) ε 1·653 ω 1·666 pale green		6–6½	194
Leucosphenite	Monoc $C2/m$	a 9·781–9·800 b 16·814–16·854 c 7·191–7·208 β 93° 16′–93° 27′ V 1180·6–1188·4		2	—	3·05–3·09	4·222 8·45 3·371 2·891 3·306 2·813	(100)*n (90) (70) (60) (50) (40)	Biax (+) α 1·640–1·648 β 1·657–1·664 γ 1·681–1·691 2V 75–79° colourless	$Y \wedge c = -3°$ to 9° $Z = b$ $r > v$	6–6½	106, 630, 770
Hyalotekite	(?)	No data		(?)	—	3·81	3·45 3·53 2·94 3·81 2·297 2·143	(100) n (80) (80) (70) (65) (65)	Biax (+) α 1·960–1·965 β 1·960–1·965 γ 1·963–1·969 2V ≈0–26° colourless	$r < v$, strong	5–5½	408, 795, 796, 799

Table III.—The Minerals of Boron arranged Alphabetically

Mineral	Composition (Table I)
Aksaite	Borate, Mg
Aldzhanite	Borate with halogen
Ameghinite	Borate, Na
Ammonioborite	Borate, NH_4
Aristarainite	Borate, Na
Avogadrite	Fluoborate, K
Axinite (Group)	Borosilicate, Ca
Azoproite	Borate, Fe and Mg
Bakerite	Borosilicate, Ca Datolite group
Bandylite	Borate with halogen
Behierite	Borate, Ta
Berborite	Borate, Be
Biringuccite	Borate, Na
Bonaccordite	Borate, Fe and Ni
Boracite	Borate with halogen
Borax	Borate, Na
Borcarite	Borate with carbonate
Braitschite	Borate, Na and Ca
Buergerite	Borosilicate, Na Tourmaline group
Cahnite	Borate with arsenate
Calciborite	Borate, Ca
Cappelenite	Borosilicate, Ca and RE
Carboborite	Borate with carbonate
Caryocerite	Borosilicate, Ca and RE
Chambersite	Borate with halogen
Chelkarite	Borate with halogen
Colemanite	Borate, Ca
Congolite	Borate with halogen
Danburite	Borosilicate, Ca
Datolite	Borosilicate, Ca Datolite group
Datolite (Group)	Borosilicate, Ca
Dravite	Borosilicate, Na Tourmaline group
Dumortierite	Borosilicate, Al
Elbaite	Borosilicate, Na Tourmaline group
Ericaite	Borate with halogen
Ezcurrite	Borate, Na
Fabianite	Borate, Ca
Ferroaxinite	Borosilicate, Ca Axinite group
Ferruccite	Fluoborate, Na
Fluoborite	Borate with halogen
Frolovite	Borate, Ca
Gadolinite (Boron bearing)	Borosilicate, Ca Datolite group
Garrelsite	Silicoborate
Gaudefroyite	Borate with carbonate
Ginorite	Borate, Ca
Gowerite	Borate, Ca
Grandidierite	Borosilicate, Al
Halurgite	Borate, Mg
Hambergite	Borate, Be
Harkerite	Borosilicate, Ca
Heidornite	Borate with sulphate
Hellandite	Borosilicate, Ca and RE
Hilgardite	Borate with halogen
Holtite	Borosilicate, Al
Homilite	Borosilicate, Ca Datolite group
Howlite	Silicoborate
Hulsite	Borate, Fe and Mg
Hungchaoite	Borate, Mg
Hyalotekite	Borosilicate, Pb
Hydroboracite	Borate, Mg and Ca
Hydrochlorborite	Borate with halogen
Inderborite	Borate, Mg and Ca
Inderite	Borate, Mg
Inyoite	Borate, Ca
Ivanovite	Borate with halogen
Jeremejevite	Borate, Al
Jimboite	Borate, Mn
Johachidolite	Borate, Al
Kaliborite	Borate, Mg
Kernite	Borate, Na
Kornerupine	Borosilicate, Al
Korzhinskite	Borate, Ca
Kotoite	Borate, Mg
Kurchatovite	Borate, Mg and Ca
Kurgantaite	Borate, Ca and Sr
Kurnakovite	Borate, Mg
Larderellite	Borate, NH_4
Leucosphenite	Borosilicate, Ba
Ludwigite	Borate, Fe and Mg
Lüneburgite	Borate with phosphate
Manandonite	Borosilicate, Li
Manganaxinite	Borosilicate, Ca Axinite group
Mcallisterite	Borate, Mg
Melanocerite	Borosilicate, Ca and RE
Metaborite	Boric acid
Meyerhofferite	Borate, Ca
'Mineral A'	Borosilicate, Ca Datolite group
'Mineral X'	Borate, Mn
Nasinite	Borate, Na
Nifontovite	Borate, Ca
Nobleite	Borate, Ca
Nordenskiöldine	Borate, Sn
Olshanskyite	Borate, Ca
Orthopinakiolite	Borate, Mn
Painite	Borosilicate, Al
Parahilgardite	Borate with halogen
Pentahydroborite	Borate, Ca
Pinakiolite	Borate, Mn
Pinnoite	Borate, Mg
Preobrazhenskite	Borate, Mg
Priceite	Borate, Ca
Probertite	Borate, Na and Ca
p-Veatchite	Borate, Sr
Reedmergnerite	Borosilicate, Na
Rhodizite	Borate, Be
Rivadavite	Borate, Na
Roweite	Borate, Mn
Sakhaite	Borate with carbonate
Santite	Borate, K
Sassolite	Boric acid
Satimolite	Borate with halogen
Sborgite	Borate, Na
Schorl	Borosilicate, Na Tourmaline group

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Table III.—(continued)

Mineral	Composition (Table I)
Seamanite	Borate with phosphate
Searlesite	Borosilicate, Na
Serendibite	Borosilicate, Al
Sibirskite	Borate, Ca
Sinhalite	Borate, Al
Solongoite	Borate with halogen
Spencite	Borosilicate, Ca and RE
Stillwellite	Borosilicate, Ca and RE
Strontioborite	Borate, Sr
Strontioginorite	Borate, Ca and Sr
Strontiohilgardite	Borate with halogen
Suanite	Borate, Mg
Sulfoborite	Borate with sulphate
Sussexite	Borate, Mn
Szaibelyite	Borate, Mg
Tadzhikite	Borosilicate, Ca and RE
Teepleite	Borate with halogen
Tertschite	Borate, Ca
Teruggite	Borate with arsenate
Tienshanite	Borosilicate, Ba
Tincalconite	Borate, Na
Tinzenite	Borosilicate, Ca Axinite group
Tourmaline (Group)	Borosilicate, Na
Tritomite	Borosilicate, Ca and RE
Tsilaisite	Borosilicate, Na Tourmaline group
Tunellite	Borate, Sr
Tyretskite	Borate, Ca
Ulexite	Borate, Na and Ca
Unnamed mineral ('Mineral A', 'Tadzhik mineral')	Borosilicate, Ca Datolite group
Unnamed mineral ('Mineral X')	Borate, Mn
Unnamed mineral (Voronova *et al.*, 693)	Borate, Ca and Sr
Uralborite	Borate, Ca
Uvite	Borosilicate, Na Tourmaline group
Veatchite	Borate, Sr
p-Veatchite	Borate, Sr
Vimsite	Borate, Ca
Volkovskite	Borate, Ca
Vonsenite	Borate, Fe and Mg
Wardsmithite	Borate, Mg and Ca
Warwickite	Borate, Fe and Mg
Wightmanite	Borate, Mg
Wiserite	Borate, Mn

Table IV.—The Minerals of Boron: Synonymy

rej.: Name rejected by the International Mineralogical Association: Commission on New Minerals and Mineral Names.
sp.: Misspelling, variant spelling or transliteration (usually from Russian or Chinese).

Synonym; variety	Mineral (Table III)
Achroite	**(Elbaite)**
Afterschorl	**(Axinite Group)**
Aksynit	**(Axinite Group)**
Alumoferroascharite	(rej.; **Szaibelyite)**
Aphrizite	**(Schorl)**
Aphryzite	**(Schorl)**
Apyrite	**(Elbaite)**
Ascharite	**(Szaibelyite)**
Ascharite-alpha	**(Szaibelyite)**
Aschentrecker	**(Tourmaline Group)**
Aschenzieher	**(Tourmaline Group)**
Ash-drawer	**(Tourmaline Group)**
Atincar	**(Borax)**
Auger's borate	**(Nasinite)**
Avogadroite	**(Avogadrite)**
Balavinskite	(rej.)
Baurach	**(Borax)**
Baurak	**(Borax)**
Bechilite	(mixture)
Bechilith	(bechilite)
Bementite	**(Danburite)**
Beta-ascharite	**(Szaibelyite)**
Bodyite	(sp.; **Probertite)**
Boracite-alpha	**(Boracite)**
Borazit	**(Boracite)**
Borocalcite	**(Ulexite)**
Boromagnesite	**(Szaibelyite)**
Boronatrocalcite	**(Ulexite)**
Boron-edenite	(boron-bearing edenite; synthetic)
Boron-phlogopite	(boron-bearing phlogopite; synthetic)
Borras	**(Borax)**
Borspar	**(Colemanite)**
Botriolite	**(Datolite)**
Botryolite	**(Datolite)**
Boydite	**(Probertite)**
Brazilian chrysolite	**(Tourmaline Group)**
Brazilian emerald	**(Tourmaline Group)**
Brazilian ruby	**(Tourmaline Group)**
Brazilian sapphire	**(Tourmaline Group)**
Breislachite	**(Vonsenite)**
Breislakite	**(Vonsenite)**
Calchydroborite	**(Pentahydroborite)**
Calcibeborosilite	**(Unnamed mineral; 'Mineral A')**

Table IV.—(continued)

Synonym; variety	Mineral (Table III)
Calciborite I	(synthetic Ca borate; not known as mineral)
Calciborite II	(**Calciborite**)
Calcium boratosilicate	(**Datolite**)
Calcium edingtonite	(**Cahnite**)
Calcium hilgardite 2M(Cc)	(rej.; **Hilgardite**)
Calcium hilgardite 3Tc	(rej.; **Parahilgardite**)
Calcybeborosillite	(**Unnamed mineral; 'Mineral A'**)
Camsellite	(**Szaibelyite**)
Cerhomilite	(cerian gadolinite?, 652)
Chaux-boratée-siliceuse	(**Datolite**)
Chrome-tourmaline	(**Dravite; Schorl**)
Chrysocolla (Agricola)	(**Borax**)
Chuntschshaoit	(sp.; **Hungchaoite**)
Cockle	(**Tourmaline Group**)
Collbranite	(**Ludwigite**)
Coronite (Hunt)	(**Dravite**)
Cotoite	(sp.; **Kotoite**)
Cotton ball	(**Ulexite**)
Criptomorphite	(**Ginorite**)
Cryptomorphite	(**Ginorite; Ulexite**)
Cuboboracite	(**Boracite**)
Cubochambersite	(**Chambersite**)
Cuboericaite	(**Ericaite**)
Cyclopeite	(**Vonsenite**)
Cyprine	(idocrase, boron bearing)
Daourite	(**Elbaite**)
Datholite	(**Datolite**)
Daurite	(**Elbaite**)
Distome spar	(**Datolite**)
Dystome spar	(**Datolite**)
Eichwaldite	(**Jeremejevite**)
Eicotourmaline	(**Tourmaline Group**)
Eisenboracit	(**Congolite; Ericaite**)
Eisenstassfurtit	(**Congolite; Ericaite**)
Enceladite	(**Warwickite**)
Erdmannite (Berlin)	(mixture)
Eremeevite	(sp.; **Jeremejevite**)
Eremeyevite	(sp.; **Jeremejevite**)
Eremyeevite	(sp.; **Jeremejevite**)
Esmarkite (Hausmann)	(**Datolite**)
Ettringite	(boron bearing)
Eukotourmaline	(**Tourmaline Group**)
Faserdatolith	(**Datolite**)
Feraxinite	(sp.; **Ferroaxinite**)
Ferroludwigite	(**Vonsenite**)
Ferrovonsenite	(**Vonsenite**)
Franklandite	(**Ulexite**)
Frolowit	(sp.; **Frolovite**)
Gadolinite	(boron bearing; **Datolite Group**)
Galurgite	(sp.; **Halurgite**)
Glasschorl	(**Axinite Group**)
Gouvernit	(sp.; **Dravite**)
Gouverneurite	(**Dravite**)
Grape-stone	(**Datolite**)
Haungchaoite	(sp.; **Hungchaoite**)
Hayesine (Bechi)	(bechilite)
Hayesine (Dana)	(**Ulexite**)
Hayesine (Forbes)	(bechilite)
Hayesinit	(sp.; hayesine)
Hayesite	(sp.; hayesine)
Haysenite	(sp.; hayesine)
Heintzite	(**Kaliborite**)
Hintzeite	(**Kaliborite**)
Hoeferite (Cipriani)	(rej.; **Biringuccite**)
Holtonite	(**Kotoite**)
Huangtsaoite	(sp.; **Hungchaoite**)
Humboldtite (Lévy)	(**Datolite**)
Hungtsaoite	(sp.; **Hungchaoite**)
Huyssenite	(**Congolite; Ericaite**)
Hyalite (Klaproth)	(**Axinite**)
Hydroascharit	(rej.; **Szaibelyite**)
Hydroborocalcite	(hayesine)
Hydrochlorbechilite	(**Hydrochlorborite**)
Hydroxyl-ascharite	(rej.; **Szaibelyite**)
Hydroxyl-szajbelyite	(rej.; **Szaibelyite**)
Idocrase	(boron bearing)
Indicolite	(**Elbaite**)
Indigolite	(**Elbaite**)
Iochroite	(**Tourmaline Group**)
Iron boracite	(**Congolite; Ericaite**)
Iwanowit	(sp.; **Ivanovite**)
Janolite	(**Axinite Group**)
Jeremeievite	(sp.; **Jeremejevite**)
Jeremeiewite	(sp.; **Jeremejevite**)
Jeremejeffite	(sp.; **Jeremejevite**)
Jeremejeit	(sp.; **Jeremejevite**)
Jeremejewit	(sp.; **Jeremejevite**)
Jochroite	(sp.; **Tourmaline Group**)
Khaulite	(sp.; **Howlite**)
Kornerupite	(sp.; **Kornerupine**)
Kramerite	(**Probertite**)
Kryptomerite	(discarded name)
Kryptomorphit	(**Ginorite**)
Kurnakowit	(sp.; **Kurnakovite**)
Lagonite	(mixture)
Lagunite	(sp.; lagonite)
Lardellerite	(sp.; **Larderellite**)
Lesserite	(rej.; **Inderite**)
Li-tourmaline	(**Elbaite**)
Lithia tourmaline	(**Elbaite**)
Lithium tourmaline	(**Elbaite**)
Ludwigite-aluminifere	(**Ludwigite**)
Lueneburgite	(sp.; **Lüneburgite**)
Lüneburger Sedativsalz	(**Boracite**)
Macallisterite	(**Mcallisterite**)
Magalborite	(**Sinhalite**)
Maghydroxyborite	(**Wightmanite**)
Magnesioludwigite	(**Ludwigite**)
Magnesiosussexite	(**Szaibelyite**)
Magnesium-axinite	(**Ferroaxinite**)
Magnesium roweite	(magnesian **Roweite**)
Magnesium-sussexite	(**Szaibelyite**)
Magnioborite	(rej.; **Suanite**)
Magniohydroborite	(**Halurgite**)
Magnodravite	(rej.; **Dravite**)
Magnohydroborite	(**Halurgite**)
Manganboracit	(**Chambersite; Ericaite**)

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Table IV.—(continued)

Synonym; variety	Mineral (Table III)
Mangan-ludwigite	**(Pinakiolite)**
Manganoaxinite	(sp.; **Manganaxinite**)
Manganseverginite	**(Tinzenite)**
Metaboracite	**(Boracite)**
Metahydroboracite	**(Inderborite)**
Metakernite	(synthetic Na borate; not known as mineral)
Micallisterite	(sp.; **Mcallisterite**)
Mineral B (Woodford, 1940)	**(Ludwigite)**
Mineral H (Woodford, 1940)	**(Tourmaline Group)**
Mineral (of Thompson and Gower, 1954)	**(Hulsite)**
Mohavite	**(Tincalconite)**
Naborosilite	**(Reedmergnerite)**
Natroborocalcite	**(Ulexite)**
Natrocalcite (Uttinger)	**(Datolite)**
Natrohydroborite	**(Borax)**
Natronborocalcite	**(Ulexite)**
Neocolemanite	**(Colemanite)**
Noceran	(sp.; **Fluoborite**)
Nocerina	(sp.; **Fluoborite**)
Nocerite	**(Fluoborite)**
Nordenskioeldite	(sp.; **Nordenskiöldine**)
Nordenskioldite	(sp.; **Nordenskiöldine**)
Octahedral borax	**(Tincalconite)**
Oisanite (Klaproth)	**(Axinite Group)**
Oisannite	(sp.; **Axinite Group**)
Olshanskyte	(sp.; **Olshanskyite**)
Paigeite	**(Vonsenite)**
Pandermite	(mixture of **Colemanite, Howlite, and Priceite; 797**)
Parasite	**(Boracite)**
Paraveatchite	**(p-Veatchite)**
Paternoite	**(Kaliborite)**
Pierrepontite	**(Schorl)**
Preobatschenskit	(sp.; **Preobrazhenskite**)
Preobrajenskite	(sp.; **Preobrazhenskite**)
Preobrazhensquite	(sp.; **Preobrazhenskite**)
Prismatine	**(Kornerupine)**
Proberite	(sp.; **Probertite**)
Raphite	**(Ulexite)**
Rasorite	**(Kernite)**
Red schorl	**(Elbaite)**
Rhodicit	(sp.; **Rhodizite**)
Rubellite	**(Elbaite)**
Sachaite	(sp.; **Sakhaite**)
Sapphirine	(boron bearing)
Sassolin	**(Sassolite)**
Schirl	(sp.; **Schorl**)
Schörl	(sp.; **Schorl**)
Schörlite	(sp.; **Schorl**)
Schorlite (Hunt)	(sp.; **Schorl**)
Schorl violet	**(Axinite Group)**
Schurl	(sp.; **Schorl**)
Sedativ-Spath	**(Boracite)**
Severginite	**(Manganaxinite)**
Sewerginit	(sp.; **Manganaxinite**)
Shorl	(sp.; **Schorl**)
Siberite	**(Elbaite)**
Sideroborine	(lagonite)
Sieberite	**(Elbaite)**
Silicoborocalcite	**(Howlite)**
Sirlesit	(sp.; **Searlesite**)
Sirlezite	(sp.; **Searlesite**)
Sjajbelit	(sp.; **Szaibelyite**)
Soda-dravite	**(Dravite)**
Stangenschorl	**(Tourmaline Group)**
Stassfurthite	(sp.; **Boracite**)
Stassfurtite	**(Boracite)**
Stiberite	**(Ulexite)**
Stiborite	**(Ulexite)**
Stillbellite	(sp.; **Stillwellite**)
Strontiohilgardite-1Tc	(rej.; **Strontio-Hilgardite**)
Strontium-ginorite	**(Strontioginorite)**
Suhr's borate	**(Ezcurrite)**
Sulphoborite	(sp.; **Sulfoborite**)
Sverginite	**(Manganaxinite)**
Szajbelit	(sp.; **Szaibelyite**)
Szajbelyite	(sp.; **Szaibelyite**)
Tadzhikite, Type I	(name?; partial description, 199)
Tadzhikite, Type II	**(Tadzhikite, 199)**
Taltalite	**(Tourmaline Group)**
Tanborite	**(Behierite)**
Thumerstein	**(Axinite Group)**
Thumerstone	**(Axinite Group)**
Thumite	**(Axinite Group)**
Thummerstone	**(Axinite Group)**
Tincal	**(Borax)**
Tincalzite	**(Ulexite)**
Tinkal	**(Borax)**
Tinkalcit	**(Ulexite)**
Tinkalite	**(Borax)**
Tinkalkonit	(sp.; **Tincalconite**)
Tinkalzit	(sp.; **Ulexite**)
Titanium lugwigite	**(Ludwigite)**
Titantourmaline	**(Tourmaline Group)**
Tiza	**(Ulexite)**
Tourmalinite	(sp.; **Tourmaline Group**)
Triclinohilgardite	**(Parahilgardite)**
Trigonomagneborite	**(Mcallisterite)**
Tritomite-(Ce)	**(Tritomite)**
Tritomite-(Y)	**(Spencite)**
Tumite	(sp.; **Axinite Group**)
Turamali	**(Tourmaline Group)**
Vanadium-tourmaline	**(Tourmaline Group)**
P-veatchite	**(p-Veatchite)**
Verdelite	**(Elbaite)**
Vesuvian (Werner)	(idocrase, boron bearing)
Vesuvianite	(idocrase, boron bearing)
Vesuvian-jade	(idocrase, boron bearing)
Viluite	(idocrase, boron bearing)
Volkovite	**(Strontioginorite)**
Wilouite	(sp.; idocrase, boron bearing)
Wiluite (Von Leonhard)	(sp.; idocrase, boron bearing)
Winkworthite	**(Howlite)**

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Table IV.—(continued)

Synonym; variety	Mineral (Table III)	Synonym; variety	Mineral (Table III)
Wolkowit	(sp.; **Strontioginorite**)	Yeremeyevite	(sp.; **Jeremejevite**)
Wurfelstein	**(Boracite)**	Yonolite	(sp.; **Axinite Group**)
Xeuxite	(sp.; **Tourmaline Group**)	Zala	**(Borax)**
Yanolite	**(Axinite Group)**	Zeuxite	**(Tourmaline Group)**

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SECTION A2

BORON GEOCHEMISTRY

BY VINCENT MORGAN

Several relatively complete monographs on the geochemistry of boron have been published. Notable among these are Goldschmidt and Peters, 1932[669]; Gmelin, 1935; Hermann Harder, 1959, 1961[495,444] (three parts); Maurice, 1966[979]; Aleksandrov, Barsukov and Shcherbina.[1199] The origin, mode of occurrence, distribution and relationship of boron with other geological materials has been the subject of much intensive investigation throughout the world during the last few decades. Additionally, several thousand papers have been published on the subject of boron. The following is an attempt to correlate the most significant of these.

THE OCCURRENCE OF BORON

Boron is a relatively rare element in the cosmos, its abundance being estimated at about 6·2 to 24 boron atoms per 10^6 atoms of silicon[672], and until quite recently it was undetected outside of terrestrial occurrences. Now, however, it is known to occur in low concentration throughout the universe, having been detected in many stars including the sun, in meteorites, moon rocks and the earth's atmosphere (including rain, snow and dust); in the waters, rocks and soils of the earth; and in life forms, both current and fossil. Part of the detection problem was the lack of sufficiently sophisticated methods for the estimation of low concentrations of boron and the interference of the earth's atmosphere in making measurements of stellar occurrences.

For the most part, the boron concentration is low, averaging perhaps 10 to 13 p.p.m. of boron in that part of the earth's crust available for investigation (atmosphere, hydrosphere and the outer ten miles of the crust).[491,660,978,987] Local concentrations of many millions of tons are known; see Concentration of Boron, p. 111.

Boron does not occur on earth as the native element, but is always combined with oxygen and a metal to form borates, borosilicates, etc.; with oxygen and hydrogen to form ortho- or meta-boric acid; with a halogen, or with oxygen and a halogen. Both hydrous and anhydrous boron minerals occur in nature; see Section A1. There seems to be no simple relationship between the number of mineral species formed by an element and its abundance. Rather the crystallochemical parameters (ionic radius, electronegativity, valence, coordination number) seem to be most important.[990,995] Boron is continually being moved about, according to what is known as the 'boron cycle'. The principal primordial source of the boron was probably the magmas. During geological time it has been carried to the earth's surface with volcanic exhalations and lavas, and through hydrothermal processes in hot springs, geysers, etc.[660,680] A greatly simplified 'boron cycle' diagram is given as Fig. 1. Actually the boron cycle is immensely more complicated; the hydrosphere consists of seas, rivers and ground waters, and the lithosphere may be subdivided into unconsolidated sediments, sedimentary rocks, metamorphic rocks, acidic, intermediate and basic magmas, and acidic and basic magmatic rocks. Boron is cycled among all of these. A number of authors have published versions of the boron cycle.[444,971,996,1036]

Refs. p. 120. Literature coverage is up to 1972

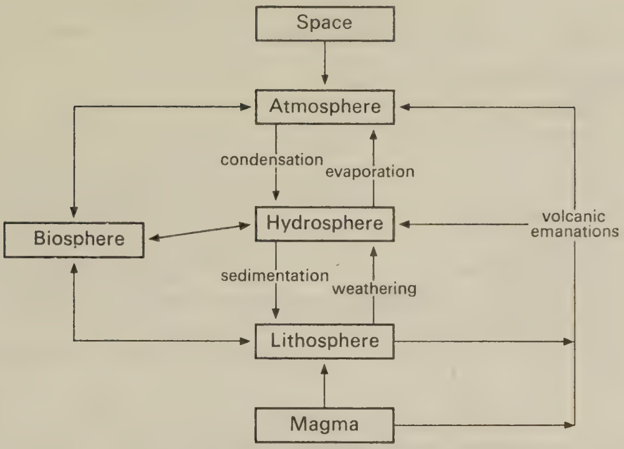

FIG. 1.—Simplified boron cycle

BORON IN SPACE

For a great many years, the presence of boron in stars and the sun was not observed.[670] More recently, with the advent of systems for making observations substantially without interference from the earth's atmosphere, such as balloon-borne, rocket-borne and satellite-borne observatories, and with the refinement of observation techniques, the presence of boron in the sun, in numerous stars, and in the space between the stars has been confirmed. The spectra due to boron vary with the type of source, the source temperature and magnetic field intensity.[28] ^{12}B has been detected in red giants[31]; spectrograms of Sirius show the presence of neutral or singly ionized boron[19], and the spectrum of Antares shows the presence of boron compounds.[21] Boron has been confirmed in spectra of sunspots and the solar atmosphere[1–3], much of the boron being present as BH and BO.[662]

The abundance of the '*L*' elements (lithium, beryllium and boron) is very much less in the stars than would be expected from the abundance of neighbouring elements in the periodic system[183, 662, 1040, 1113], producing what is termed the '*L*-element anomaly'; see Fig. 2. This is attributed in part to the ease with which their nuclei are disintegrated during nucleon genesis[673] by processes occurring at high temperatures of stellar interiors[10], to the destruction of boron by proton collision, etc.[4, 20, 27, 662] Boron is apparently formed by several mechanisms in different types of stars[183]: by proton capture by lighter elements in hot stars with a temperature greater than 20×10^6 K[4, 16], and by spallation reactions from carbon, nitrogen and oxygen in hot spots in stellar atmospheres of nuclear stars[15] and magnetic stars.[10, 18] Theoretical energy considerations require a source for '*L*' elements (lithium, beryllium, boron) other than autogenetic, each atom requiring an energy of formation equivalent to the acceleration of about 1 erg of fast protons, which energy is unlikely to be available in a star of type T-Tauri, for example, but would be available in strong cosmic-ray sources, such as supernovæ, pulsars, flare stars, etc.[661] The variation of light intensity of the Cepheid variable stars has been ascribed in part to protonic reactions with boron.[5]

Recent high-altitude cosmic-ray observations have confirmed the presence of boron nuclei in outer space[6–9, 11–14, 17, 25, 29, 32], with up to 1000 times the expected abundance based on stellar observations[12], and at kinetic energies greater than $1{\cdot}5 \times 10^9$ eV, up to 2×10^5 times the general thermal abundance for the '*L*' elements considered together.[17] The relative abundance of boron in primary cosmic radiation, relative to all nuclei heavier than 2, at these same energy levels, has been established as 7·4 to 11·9%, and relative to carbon as 24·6 to 47·4%.[17] Most of the '*L*' elements

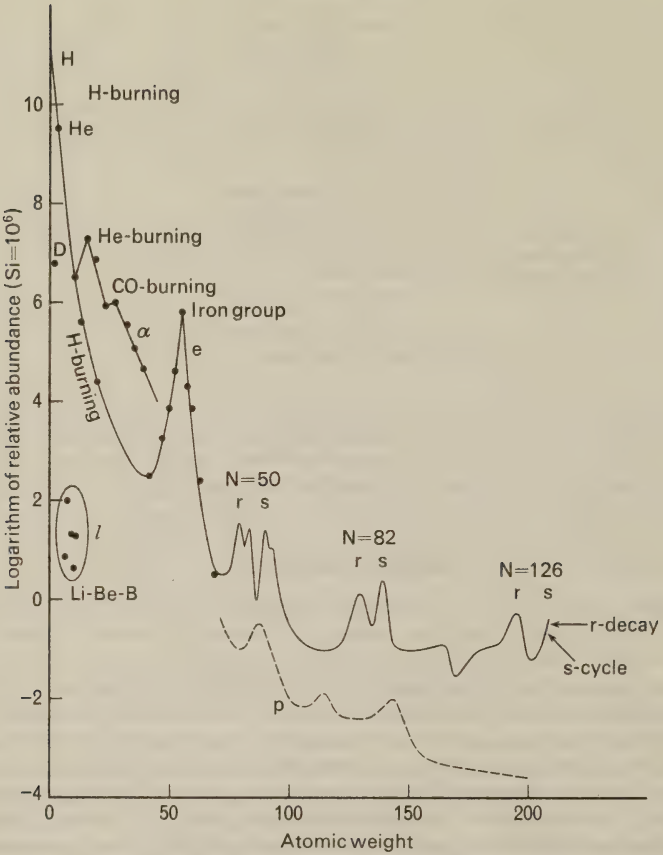

FIG. 2.—Schematic curve of atomic abundances as a function of atomic weight, based on the data of Suess and Urey[1040], as given by Fowler.[183] The '*L*' elements are circled

may have been made during an initial period of intense stellar activity by strong sources such as supernovæ, pulsars, flare stars, etc., and largely diffused in space.[661]

Prior to the Apollo space programme, the only 'in hand' evidence of the composition of extra-terrestrial matter was from the analysis of meteorites.[1063] Those known as the chondrite variety of aerolites (stony meteorites) show by far the greatest percentage of observed falls, are reasonably uniform in chemical composition and are believed to be more representative of planetismal matter than are the other meteorite varieties.[23–4, 660]

Recent boron determinations on a number of meteorites, using a newly developed fluorometric analytical method sensitive to about $\pm 1 \times 10^{-9}$ g of boron, gave the values shown in Table I. All boron determinations were made in quadruplicate, with duplicate blanks.[739]

Other investigators have reported values averaging 1·8, 2·7, 5·2 and 7·1 p.p.m. boron for chondrites[663, 664, 673], and less than 0·04 to 1·6 p.p.m. boron for the iron varieties, with the boron concentrating with the nickel.[22, 662] It has been suggested that the differences in boron content of the chondrites (including carbonaceous chondrites) and other types of meteorites may be due to differences in the mode of formation.[23, 673] The average boron content of all types of meteorites considered together has been estimated to be 1·5 p.p.m.[662] A series of 25 tektites, which may or may not be meteoritic in origin, range from 6·1 to 53·0 p.p.m. boron and average 21·8.[1038]

Analysis of rock samples returned by Apollo 11 from 'Tranquillity Base' on the moon gave the results in Table II. These values are in general agreement with the boron concentration found in many rock types on earth.

Table I.—Boron Content of Meteorites. (Condensed from Table II, Ref. [739]*)*

No. of meteorites	Type	Boron content, p.p.m.	
		Range	Average
25	Bronzite chondrites	0·14 to 5·95	1·24
24	(Same, but with highest value omitted)	0·14 to 2·36	0·82
10	Hypersthene chondrites	0·14 to 1·70	0·74
4	Achondrites	0·34 to 1·08	0·71
4	Carbonaceous chondrites	5·60 to 9·63	7·76
2	Enstatite chondrites	0·43 to 0·77	0·60
10	Bronzite chondrites with light-dark structure	0·12 to 1·57	0·54
2	Iron	0·02 to 0·03	0·025

Table II.—Boron Content of Lunar Materials

Type of rock	A	B	C	D	
Characteristics	Fine-grained vesicular	Coarse-grained crystalline	Breccia	Soil	Reference number
Analytical Method					
Emission spectrography*	N.d.	N.d.	N.d.	N.d.	666
Fluorescence	0·8	0·7, 1·2	—	1·03	665
Mass spectrometry	1, 4, 4	2, 9	2, 3	2	667

* Lower limit of detection was 10 p.p.m. B (13 samples).

BORON IN THE EARTH'S ATMOSPHERE

Data on the boron content of the earth's atmosphere are scarce, the determination apparently having been made only in recent years. Rain and snow have now been shown to contain all of the major and some of the minor inorganic constituents of ground-water, including boron.[39, 674] Most of the boron is present as orthoboric acid, H_3BO_3[48], and is associated with atmospheric moisture. Various sources for the boron have been suggested; these include sea spray[37], volcanic and hot-spring emanations, airborne dust[39, 675], industrial pollution, smoke, exhalations of plants, etc.[37, 48] Probably all of these contribute, but the greatest source seems to be actual evaporation of boric acid from sea-water, in which there is an appreciable boric acid vapour pressure. The condensate from sea water evaporated at low temperatures contains boric acid in about the same concentration as that found in river waters in areas of low boron ground concentration, such as the Pacific north-west region of the United States, but it contains no chloride.[48, 52]

The atmospheric boron content shows a wide variation from place to place, and sometimes from time to time at the same place. For example, in France in 1955 the boron content of rain varied from 0·002 to 0·0045 mg of boron per litre[33], which is one-fiftieth to one-twentieth of the 0·1 mg of boron per litre reported from Japan for both rain and snow.[34–36, 38, 105] This large variation in the boron content of rain and snow in geographically diverse locations is due at least in part to the temperature variation of the sea from which the water (and boric acid) evaporated.[52] Some investigators report that the boron content of rain decreases with time during a rainstorm[38], while others state that the boron content of the rain, unlike the chloride content, shows no regular pattern.[37, 674] The B/Cl ratio reported for rainfall in Japan at various times and places ranges from 27×10^{-4} to 420×10^{-4}, about 12 to 180 times the B/Cl ratio for sea water, which is nearly constant at $2{\cdot}25 \times 10^{-4}$.[38]

The boron carried to the earth's surface by rain and snow contributes to the boron content of the soil. One investigator calculates that the boron content of rain falling in France ranges from 13 to 30 g of boron per hectare per year, which is about one-fifth of the boron uptake of intensively cultivated crops.[33]

Boron has been found from ground level to extreme heights. A rocket-borne mass spectrometer recorded the presence of ^{10}B at heights of 100 to 210 km; this boron originates from cosmic radiation from deep space.[30]

BORON IN THE HYDROSPHERE

The hydrosphere, consisting of all the 'watery' parts of the earth, may conveniently be divided into several parts for ease of treatment. These are the seas and oceans, rivers and fresh-water lakes, saline lakes, continental ice, and ground waters of various types.[662] These will, for the most part, be considered separately.

Boron in the Sea

About 98% of the earth's water is in the world ocean, leaving only about 2% for all other waters. The total amount of ocean and sea water has been estimated to be about $1{\cdot}37 \times 10^9$ km^3 [660], which, using Clarke's mean density of 1·03 [671], gives a total weight of $1{\cdot}41 \times 10^{16}$ tons, of which about 96·5% is water and 3·5% is dissolved salts. Of this total, boron makes up about 0·014%, giving approximately 7×10^{12} tons of boron in the world ocean[61], or equivalently about 40×10^{12} tons of H_3BO_3. Orthoboric acid is the form in which most of the boron is present in sea water[44,48,60,63], although some is also present in the form of organic complexes.[40,51,53,1133] The inorganic boron concentration in sea water varies in nearly direct ratio to the salinity the world over, being about 0·00024 g of boron per g of total halogen expressed as Cl[49,50,58,64,680,1041,1045], with wt. B/wt. Cl = 0·000225 [38] and wt. B/wt. Br = 0·014.[626] Boron has been reported as making up about 0·014% of the total salts in the ocean[680,1047], but there are local anomalies.[45] The actual boron concentration varies from about 0·5 mg boron per kg of water in the Baltic Sea[43] to about 9·6 mg boron per kg of water in the Mediterranean Sea[63], perhaps higher elsewhere, and averages about 4·6 mg boron per kg of water[274], which, as expected, is much higher than for any river.[47,317] Some higher values for sea water samples were reported in 1914 and 1920[63,669], but these high values may have been due to inaccuracies in the analytical methods employed. Many boron determinations have been made on sea water; some typical values are given in Table III.

During geologic time, approximately 600 g of crustal rock, containing about 2 mg of boron, has been weathered for each kilogram of water in the world oceans.[669] For a salinity of 3·5% or 35 per mil, the boron concentration is 4·7 mg of boron per kg of water. Thus, the total boron in the sea is 240% of that which could have accumulated from the weathering of crustal rocks alone.[1041] This 'boron surplus' must then have come from sources other than rock weathering, such as volcanic eruptions, or may have been present as a volatile constituent of the primordial atmosphere of the earth.[669] Boron is continually being added to the sea by rivers and volcanoes and is just as continually removed, maintaining a nearly constant boron: salinity ratio over many millions of years.[46,314,678,754,763] The sources of the boron being added include rivers, springs, marine volcanoes, rain, dust, etc. The total boron entering the sea from continental drainage alone has been estimated at $4{\cdot}0 \times 10^8$ kg of boron per year.[578] The boron concentration of the sea is neither increasing nor decreasing[61], therefore boron must be constantly removed in order to maintain equilibrium. It is now known that the hydrous clay-mica *illite* adsorbs boron from sea water in direct ratio to the boron concentration in the sea water, thus removing boron as sediments are formed.[61,319,678,772] About $3{\cdot}3 \times 10^8$ kg boron per year are removed by this clay (illite) adsorption, about $0{\cdot}3 \times 10^8$ kg are removed by biogenic processes and $0{\cdot}4 \times 10^8$ kg are removed by other processes thus maintaining a constant boron balance.[678]

Table III.—Boron in Sea Water

Area	mg B/kg H_2O	B/Chlorinity*	References
IAPO Standard Sea Water	5·49	0.00024	676, 1046
N.E. Pacific, beyond Continental Shelf	4·56	0·000242	40
Same, including Contin. Shelf waters	4·17	0·000243	40
Between Calif. and Hawaii; near Florida	4·50	—	41
North Atlantic Coast of U.S.	4·75	0·00024	42
Baltic Sea	0·52 to 1·6	0·000264	43, 906
Mediterranean Sea	9·57	—	62
'Seas around U.S.S.R.'	4·02	0·000242	47
Various European	0·82 to 4·8	0·000233 to 0·000248	49
Barents Sea	3·8 to 4·1	0·000246 to 0·000259	53, 906
Various	—	0·00024	50
Western Pacific	4·73	—	54
Pacific	4.57	0·00024	52
India	2·2	—	55, 56
Urado Bay, Japan	4·73	0·000225 to 0·000244	58
Aegean Sea, near Santorin Volcano	4·9 to 5·5	—	819, 820
Average of all oceans	4·6	0·00024	274, 626, 1041

* Chlorinity is defined as the mass of silver required to precipitate the total halogen in 1 kg of sea water, converted to its chlorine equivalent.[1046]

There has been a virtually constant boron:salinity ratio in the sea for many millions of years, as noted above; since boron is adsorbed by the illite fraction in constant ratio to its concentration in the sea water, it is possible to determine the salinity of the sea at the time of deposition of marine sediments (paleosalinity) by determining the boron content of the illite fraction of the sediments.[60, 263, 309, 319] A Knudsen type of equation derived to show this relationship is:

$$S = 8B-1,$$

where S is the salinity in parts per thousand (per mil) and B is the boron content in parts per million.[60]

A retained atmosphere concept would require the existence of a hypothetical primordial ocean with at least 20 times as much boron as is currently found. Paleosalinity studies indicate that the boron content of the world ocean has remained relatively constant for the last two to three billion years; a gradual accumulation of both boron and water by out-gassing of the earth's interior is more in line with geologic evidence.[61]

Marine life concentrates boron by factors as great as 200, the highest reported concentration being found in the plants *Zostera nana* (910 mg B/kg), and *Z. marina* (750 mg B/kg), with marine animals showing less concentration (about 1·5 to 16 mg B/kg); most marine plants contain about 0·01% of boron dry basis.[40, 47] The shells of some marine animals contain a considerably higher boron concentration[40], e.g. up to 1870 mg B/kg for *Hydrocorallina sp.* Certain Paleozoic brachiopod shells contain 30–600 p.p.m. of boron[307]; recent marine mollusc shells showed a higher boron content in the aragonitic parts of the shells than in the calcitic parts.[272] This concentration of boron by marine organisms, and their subsequent inclusion in marine sediments, produces oozes and rocks notably higher in boron content than the parent sea; see marine sediments, below. The hard parts of marine animals are often preserved in the sediments as fossils. Just as the boron content of the illite fraction of the sediments can be used to estimate the salinity of the water in which the sediments were laid down (above), the boron content of the animal fossils can be so used. This dual relationship provides a means of paleosalinity verification. A fossil boron content greater than 0·011% B indicates marine fossils, 0·008 to 0·011% B indicates brackish water conditions, and less than 0·008% B indicates fresh-water fossils.[59]

The boron present as boric acid in sea water has several functions. Besides being necessary for the metabolism of many organisms, it is a chemical buffer, controlling the pH within narrow limits, thereby having an important role in the maintenance of the alkalinity equilibria between carbon dioxide, carbonates and bicarbonates in the sea water[662, 677], and either directly or indirectly influencing the sedimentation process.

Under suitable conditions, such as at sea-water desalinization plants or sea-salt plants remote from commercial boron sources, the bitterns could yield boron (and other) salts economically.[679]

Boron in Rivers and Streams

The boron content of the water of many rivers and creeks is extremely variable, both with time at a given place and with distance from source to mouth. The reasons for these variations are numerous, but the following are particularly significant:

(a) The variation of the boron content with time at a given station reflects the fluctuation of stream flow, due primarily to changes in the weather.[69, 668]

(b) The boron concentration from place to place along a given stream increases because of the introduction of boron-bearing waters from springs and volcanic emanations[100], decaying vegetation[106], and boron-bearing soils and rock formations[125, 807], and because of evaporation from the stream surface[69]; it decreases by reason of dilution with water of lower boron content and by removal of boron by co-precipitation with hydroxides.[69] In many areas, the flow from springs is relatively constant throughout the year, the flow-limiting factors being largely independent of time and the weather[668], whereas surface runoff is highly dependent on the weather.

The boron content of most river water is about 1/350 that of sea water.[1070]

U.S. Department of Agriculture Circular No. 7, 1944, classifies waters according to their mineral content and suitability for irrigation as shown in Table IV.[1032]

Table IV

Class	p.p.m. Dissolved solids	% Na*	Boron content, p.p.m.	Conductance $K \times 10^5$ at 25°C
1	Under 700	Under 60	Under 0·5	Under 100
2	700 to 2000	60 to 75	0·5 to 2·0	100 to 300
3	Over 2000	Over 75	Over 2·0	Over 300

* Proportion of Na to sum of Na + Ca + Mg + K, as equivalents per million, multiplied by 100. The total dissolved solids is approximately equal to $7K \times 10^5$.

A description of the three classes is as follows:

Class 1 water, excellent to good. Suitable for most plants under most conditions.
Class 2 water, good to injurious. Harmful to sensitive crops.
Class 3 water, injurious to unsatisfactory. Harmful to most crops and unsatisfactory for all but the most tolerant.

A detailed study of water quality criteria has been published by the State of California.[1049]

A number of studies of the boron content of surface streams have been made during recent years, mostly in conjunction with agricultural developments, owing to the recognition of the important role of boron in plant health. One of the early studies was that published in 1931 on the City of Los Angeles water supply from the Owens River (plus several other Southern California streams not a part of the above water supply system), whose waters were used for farm irrigation.[100] Some of the results of this study are given in Table V.

Table V.—Variation of the Boron Content (in p.p.m.) of Irrigation Waters with Time[100]

Year and month	Sampling station							
	Owens River					Other streams		
	1	2	3	4	5	6	7	8
1928								
Aug.	0·47	0·39	0·39	0·64	0·65		2·48	1·52
Sept.	0·56	0·46	0·59	0·66	0·57	0·23	2·61	1·40
Oct.	0·77	0·64	0·64	0·58	0·66	0·22	3·19	1·65
Nov.	0·87	0·66	0·86	0·61	0·62	0·23	3·29	1·50
Dec.	0·68	0·63	0·60	0·56	0·66	0·21	2·04	1·35
1929								
Jan.	0·80	0·71	0·74	0·67	0·64	0·26	2·09	1·56
Feb.	0·78	0·67	0·74	0·68	0·67	0·20	0·98	1·38
Mar.	1·26	0·90	1·20	0·74	0·71	0·24	0·91	1·40
Apr.	0·96	0·76	0·80	0·73	0·73	0·18	0·81	1·39
May	0·78	0·65	0·62	0·81	0·80	0·15	1·53	1·39
June	0·72	0·56	0·52	0·73	0·78	0·08	1·88	1·68
July	0·55	0·40	0·40	0·68	0·66	0·14	1·98	2·21
Aug.						0·14		
Mean	0·77	0·62	0·67	0·67	0·68	0·19	1·98	1·54

Key to sampling stations:
1. Los Angeles Aqueduct, heading near Aberdeen, Calif.
2. Los Angeles Aqueduct, Alabama Gates, near Lone Pine, California.
3. Los Angeles Aqueduct, North Haiwee, near Olancha, California.
4. Los Angeles Aqueduct, South Haiwee, near Olancha, California.
5. Los Angeles Aqueduct, San Fernando Powerhouse.
6. Colorado River at Yuma, Arizona.
7. Sespe Creek, California, at Diversion Dam 4·5 miles above its mouth.
8. Piru Creek at Diversion Dam above Piru, California.

Stations 1 to 5, inclusive, are along the same stream, with various tributaries in between, but little, if any, water enters the system between stations 3 and 5. There is, at times, considerable evaporation, particularly from the Haiwee Reservoir, between stations 3 and 4.

Similar studies have been made on many rivers. For instance, a study made on August 8 and 9 in 1955 showed that the Saale River in East Germany increased from 0·024 mg per litre of soluble boron at the headwaters at Eichicht to 0·200 mg per litre of soluble boron at Calbe-Ost, by dissolution of boron from formations through which it passes; this is more than an eight-fold increase.[668] Subsequent dilution at the junction with the Elbe reduced the boron concentration to 0·096 mg of boron per litre.

A particularly interesting study was made in 1969 of the hydrographic net of the Rio Bermejo (or Vinchina) in La Roja province of Argentina.[1027] Here, it was found that sufficient boron was being introduced into the river to damage agricultural crops, particularly grape vines, by various tributaries above the large fresh-water springs at La Ramadita and vicinity, upstream from Villa Union. The boron content ranged from a high of 4·47 mg of boron per litre (about nine times the permissible limit) in the Rio Punilla, near the headwaters, to 1·03 mg of boron per litre just above the fresh-water springs, and was reduced to 0·47 mg of boron per litre below the springs, considered a safe level for the crops involved. Upstream from the Ramadita springs the river water must be supplemented by well water of lower boron content in order to avoid boron damage to crops.

In some places, the boron content of a particular tributary has been found to contribute a substantial portion of the boron in a stream. At times, this causes difficulties, especially during times of low main-stream flow, when run-off water is at a minimum and the boron content of the tributary causes the boron content of the main stream to exceed permissible limits.[116] This is the situation with Mammoth Creek (which becomes Hot Creek along its lower portion) in the Owens Valley of California (a tributary of Owens River), whose waters formerly entered Los Angeles Owens River water supply, a portion of which was used for citrus irrigation. The problem here was solved originally by excluding the waters of the offending tributary, and later by impounding during periods of low main-stream flow and slow release during times of high main-stream (run-off) flow.[115] Details are shown in Table VI, referring to a period of unrestricted tributary flow.

Table VI.—Tributary versus Main-Stream B-Content[100]

Sample No.	Location	Flow cubic ft per sec	Conductance, K × 10^5 at 25°C	Boron content, p.p.m.
99	Owens River above junction	100	21·1	0·41
101	Upper Mammoth Creek	15	9.8	0·02
100	Lower Mammoth Creek	30	8·8	0·08
98	Hot Creek	35	59·1	2·32
93	Owens River below junction	—	37·1	1·00

Exclusion of the waters of Hot Creek reduces the main-stream boron content to a satisfactory level. Many similar studies have been made in recent years in various parts of the world.[26, 69, 76, 88, 97, 100, 104, 106, 125, 127, 133, 235, 294, 375, 376, 696, 712, 730–3, 735–6, 799, 807, 1020, 1021]

The U.S. Geological Survey has published an extensive and, since 1941, continuing annual series of reports on the quality of the water in streams of the United States.[730, 731, 1006, 1047] The only streams in the U.S. showing a boron content of 1 p.p.m. or greater at any time of the year are located in Utah, Arizona and California. Of these sixteen streams, three showed a boron concentration of 1 p.p.m. or greater throughout the year, while the remainder varied widely. All of the streams with a high boron content are alkaline.[1006] The boron content of the waters of these sixteen streams is given in Table VII below. Data are for 1964, the latest available at the time of writing.

Table VII.—Streams in Western U.S. which showed a Boron Content of 1 p.p.m. or greater at any time during the year 1964.[1006]

Place of sampling	Boron content, p.p.m.	pH
Duchesne River near Randlett, Utah	0·25–1·7	8.0
Gila River below Gillespie Dam, Arizona	0·26–3·6	8·0
Lost Creek at mouth, near Aurora, Utah	3·3*	7·3
San Benito River near Willow Creek School, California	1·2–2·9	8·6
Arroyo Valle near Livermore, California	0·4–1·8	8·1
Salt Slough near Los Banos, California	0·4–3·9	8·0
San Joaquin River at Fremont Ford Bridge, California	0·3–2·3	8·1
San Joaquin River near Patterson, California	0·1–1·2	8·0
Italian Slough at Clifton Court Bridge near Byron, California	0·0–3·2	7·9
Indian Slough near Brentwood, California	0·2–2·7	8·5
Cache Creek near Lower Lake, California	0·5–1·1	8·1
North Fork Cache Creek near Lower Lake, California	1·2–5·7	8·5
Cache Creek near Capay, California	1·0–3.2	8·4
Outlet Creek near Loganvale, California	0·1–2·3	8·1
Hot Creek, California	0·8–2·9	8·5
Little Hot Creek, California	7·5–11·2	9·1

* Only 1 analysis.

The mean boron content of all North American and Norwegian rivers is 0·0116 mg of boron per litre.[1020]

The rivers of the Soviet Union have been extensively analyzed for many minor constituents including boron. A condensation of some of the published literature is given in Table VIII below. Each basin shown receives the flow of several rivers.

Table VIII.—Boron Content of the Major Rivers of the Soviet Union.[1074]

Rivers flowing into:	Boron content, p.p.m.	Tons of boron/year
Baltic Sea	0·009–0·030	2,060
Black Sea and Sea of Asov Basins	0·013–0·081	5,200
Aral-Caspian Basin	0·033–0·096	19,800
Barents and Beloye Sea Basins	0·009–0·022	5,120
Kara Sea Basin	0·011–0·022	18,400
Laptev, East Siberian and Chukchi Sea Basins	0·010–0·015	12,300
Bering, Okhotsk and Japan Sea Basins	0·005–0·009	7,500
Total for territory of the U.S.S.R.		50,600

In general, fresh-water systems retain most of their inorganic boron content, except that which is precipitated as hydroxides or removed by organisms, until the water reaches the sea, whereupon changes in salinity and pH promote boron removal by incorporation into suspended silicates.[678] It has been estimated that the mean boron concentration of all rivers draining the Soviet Union and North America is 0·012 mg of boron per litre. With a total world influx of $3·3 \times 10^{16}$ litres of fresh water per year,

Table IX.—Changes in the Boron: *Chloride Ratio during One Year.*
(*Values expressed as* ‰B × 10^3/‰Cl, *are read from a plot.*[106])

Year and month	Sampling station								
	1	2	3	4	5	6	7	8	9
1955									
Apr.	3·5	13·8	0	2·1	8·0	3·7	3·0	0·2	0·5
May	3·9	18·2	1·0	4·1	5·5	3·2	4·5	1·2	0·7
June	4·2	10·2	2·0	0	4·5	3·5	5·5	2·2	0
July	5·4	4.5	0·4	3·6	6·3	3·1	3·2	2·2	0
Aug.	8·1	4.5	1·4	4·5	5·1	3·7	3·0	1·8	0·2
Sept.	9·8	7·2	6·8	8·4	4·7	4·1	3·2	1·6	0·1
Oct.	6·0	3·1	3·1	7·6	6·5	1·0	1·0	3·9	0·2
Nov.	7·2	4·2	2·0	9·0	5·5	1·0	5·2	2·0	0·3
Dec.	3·0	3·5	0·4	0·4	8·2	2·1	3·0	4·1	0·2
1956									
Jan.	3·2	5·2	3·4	4·5	7·1	2·0	2·6	1·3	0·2
Feb.	3·8	1·8	4·0	9·2	7·3	3·1	1·5	3·0	0·2
Mar.	4·8	2·5	3·0	3·0	5·7	3·0	1·4	4·1	0·2

Key to sampling stations:
1. Raccoon River at Des Moines, Iowa.
2. San Juan River near Blanco, New Mexico.
3. Cedar River at Cedar Rapids, Iowa.
4. Iowa River at Iowa City, Iowa.
5. Republican River at Max, Nebraska.
6. Canadian River near Sanches, New Mexico.
7. Animas River at Farmington, New Mexico.
8. Kiryu River, Japan.
9. Colorado River near Glenwood Springs, Colorado.

A number of other publications give similar data.[69, 101, 106, 125, 133, 696, 712, 731, 733, 1006, 1047, 1074] the total annual boron entering the sea from all continental drainage is approximately 4×10^{14} mg per year[678] (equivalent to 4×10^8 kg/year). Since the boron content of the sea remains virtually constant over millions of years (see Boron in the Sea, above), the same amount must be removed from the sea by vaporization and by inclusion in marine organisms and sediments. The recent annual world consumption of boron, mostly in the form of borates, has been estimated to be 400,000 tons of B_2O_3[660], equivalent to about $1{\cdot}25 \times 10^8$ kg of boron. Thus, the boron entering the sea annually from all continental drainage is more than three times the estimated total yearly world production for industrial and agricultural uses.

While the weight ratio of boron to chlorinity in the sea is very nearly constant the world over, at about $0{\cdot}240 \times 10^{-3}$ (see above, sea-water section), this ratio in rivers and streams is highly variable, and usually much greater.[106, 668] An example is given in a recent publication showing this ratio for nine rivers (eight in U.S., one in Japan) over a one-year period. The data appearing in Table IX were approximated by estimation from a plot.

Boron in Groundwater

As used here, the term 'groundwater' refers to any sub-surface water, and includes flowing springs (both hot and cool), geysers, aquifers (both flowing and confined), oilfield brines, etc. These waters may be predominantly connate[30, 90], largely recent, or may contain a high percentage of juvenile water. The sources of the boron in these waters include ancient brines, leaching of sedimentary rocks, hot-water or steam leaching of volcanic rocks or magmas, etc.[23] Groundwaters have been classified in diverse ways, such as geological, physical, or chemical, by different authors. Clarke[671] classifies such waters chemically according to their negative radicals, and lists the following types: chloride, sulphate, carbonate, acidic, mixed, and unusual combinations, including nitrates, borate, sulphide and silicate. The total mineral content of groundwater varies greatly, from virtually no dissolved solids to concentrations much greater than those found in sea water; the above classifications overlap to a considerable extent. The reported boron content ranges from 0 to more than 1000 mg of boron per litre (see Table X). In some groundwaters the boron content is related to the salinity, as in sea water[33], whereas in others it is proportional to the HCO_3^- content.[13, 16] This reflects the origin of the contained salts, i.e. whether they were leached from sediments or related to volcanism etc. For convenience of discussion, the following subdivisions will be used here: springs of all kinds, including geysers and soffioni; relatively shallow wells, such as used for irrigation water sources; deep waters (non-oilfield brines) and oilfield brines.[1]

White *et al.*[1126] give a comprehensive series of tables of analyses of many subsurface waters classified according to water type.

Boron in Mineral and Spring Waters

Mineral springs and wells are of many types, such as steam, thermal, cool, acidic, neutral, alkaline, saline, carbonate, etc. The waters issuing from springs may be predominantly connate, largely recent, or may contain a high percentage of juvenile water.[30, 90, 671] While boron is known to be present in the waters of springs all over the world, the major commercial boron deposits, as well as spring mineralizations, are to be found along the well-known 'ring of fire' around the Pacific Ocean, along one north-east to south-west belt across Siberia and through India, and two (or perhaps three) east-west belts across Eurasia[885, 1035], or along known or postulated abyssal fractures.[975] This gives credence to the idea that the occurrence of boron is associated with volcanism, but does not necessarily define the source of the boron. Where the boron:chloride ratio is essentially the same as for sea water, the source of the boron is almost certainly buried marine evaporites or ancient brines.[93] Where the boron: chloride ratio is considerably higher than for sea water, thus eliminating marine evaporites as the source, other possibilities must be considered; in many of these waters the boron content is proportional to that of bicarbonate.[75, 77] For a long time, the probable source was thought to be exclusively magmatic[662], but recent experiments have shown that boron (and other elements) can be leached from various types of igneous, metamorphic and sedimentary rocks by water at 100° to 600°C at pressures up to 1500 bars.[478, 703, 757, 1029, 1033] Thus the source of the boron in springs

Table X.—Boron Content of Mineral Springs

Name	Location	Boron content, mg/litre	Reference
Arrowhead Hot Springs	California	2·6	100
29 Springs, various	California	0·9 to 372	1044
35 Springs, various	Calif., Nev., Mex.	0·09 to 11·5	1043
Aqua de Ney	California	240	130
Herman Pit	Sulphur Bank, Calif.	660	1034
Sespe Hot Springs	California	6·7 to 12·5	100
Tuscan Spring	California	201	1126
Wilbur Spring	California	432	1126
Various High-borate springs	California	13 to 530	1126
Steamboat Springs	Nevada	72	671
Stinking Spring	Utah	60	1126
5 Springs	Yellowstone National Park	5 to 11	671
Saratoga Spa	New York	0·4 to 5·8	75
8 Springs	Mexico	<0·1 to 2·8	701
Tokaanu	Lake Taupo, New Zealand (alkaline)	28 to 82	86
Near Tokaanu	Lake Taupo, New Zealand (acidic)	0·9 to 24	86
Near Tokaanu	Lake Taupo, New Zealand (steam)	12 to 43	86
Ngawha Hydrothermal Area	N. Island, New Zealand	0 to 1085	704
Ketetahi Hot Springs	New Zealand	up to 346	485
5 Thermal springs	Umnak Island	20 to 50	471
Various	Kamchatka and Kuriles	15 to 75	92
42 Springs	Nana Shiguri and Jyohoji, Japan	up to 770	72
55 Springs	Eastern Japan	0·025 to 773	70
44 Springs	Hatimandai, Japan	0·9 to 190	73
Kawaharayu Hot Springs	Japan	8·75	69
Isobe (6 springs)	Gumma, Japan	300 to 400	74
Beppu Hot Springs	Japan	2·5 to 12	77, 78, 79
Ashidate Spa	N.E. Japan	5·5	80
Aone No. 1 and No. 2	N.E. Japan	2·8, 2·4	80
Osoreyama Hot Springs	Aomori Prefecture, Japan	13 to 384	706
105 Springs	Hokkaido, Japan	0 to 58	82
5 Springs	Hokkaido, Japan	over 58	82
Bad Hall	Austria	42	1126
Various	Czechoslovakia	33 to 119	980
Cheleken Hydrothermal Waters	Turkmenia	11 to 46	740
Kapobi Spring	Source of Chveshuri River, Caucasus	562	71
19 Springs	Caucasus	23 to 388	230
4 Springs	White Russia	2·0 to 3·9	88
20 Springs	Various, Soviet Union	0·15 to 62	255
Thermal Waters	Vicinity of Mendeléev Volcano	0·3 to 13·5	813
Various Carbonic	Armenia	0·5 to 100	240
23 springs, associated with volcanism	Worldwide	0·6 to 900	249
'Many'	Romania	29 to 219	87
52 Waters	Transylvania	0 to 166	1031
Various geysers	Tuscany	av. 55	462
17 Thermal waters	Tuscany	0·5 to 53	451
22 Soffioni	Tuscany	39 to 161	453, 454
Various	Ireland	0·7 to 13	1126

Additional data may be found in references [87, 98, 104, 109, 110, 455, 461, 470, 472, 483, 653, 692–5, 697–700, 702, 705, 727] remains enigmatic; it could be primary, as from magmas[82], or it could be the result of hydrothermal leaching of older rocks. It is likely that both processes occur.

Concentrations of more than 1000 mg of boron per litre have been found in a few springs not associated with known borate deposits; see Table X. Many of the springs with a high boron content are thermal, but likewise, many are cool. For example, on the mainland of Japan, all of the springs with a high boron content are cool springs, and on Hokkaido 40% are cool.[70] In New Zealand, on the other hand, all high-boron springs are warm or hot.[86,485] The cool springs of Japan seem to be different in type from the hot springs.[70] Those with the highest boron content are acidic, indicating a geochemical relationship with bicarbonate.[10] There is some evidence that at least some springs which are cool at the surface are hot at depth.[975] The high-boron-bearing springs throughout the world are of varying degrees of alkalinity, ranging from a pH of 11·6 for Aqua de Ney spring in California[130] to 6·0 for one of the acidic springs of Japan.[72] In some areas, the concentration of trace elements, including boron, increases with increasing temperature.[73,74,79] The relationships between the boron content and other properties of the waters have been discussed by a number of authors.[70,72–5,77,79,82,84,90,92,93,114,134,246,707] In Table X are listed many of the mineral springs of the world for which an analysis of the boron content has been published; no doubt there are many more. No effort has been made to group them according to type or degree of mineralization, but they are arranged roughly by geographical area.

Many of the springs are at existing or potential health resorts or spas. The 'soffioni' of the Tuscany area in Italy have been extensively studied, and have been highly developed to utilize the hydrothermal energy for the production of electricity and for the production of boric acid from the condensate. The vapours from the soffioni also contain a large percentage of carbon dioxide, and measurable quantities of helium, neon, argon, xenon, ammonia and nitrogen, as well as hydrogen sulphide, hydrogen, methane and other combustible gases.[453,463,989]

Boron in Irrigation and Domestic Well Water

The presence of boron in the water of wells used for irrigation and domestic supply has assumed importance because of the recognized deleterious effect of excessive

Table XI.—Boron in Irrigation and Domestic Wells

Location of wells	Boron content, p.p.m.	Reference
Burnt River Valley, Oregon (2 wells)	2·3 to 3·6	721
Putah Creek Basin (near Sacramento) California (47 wells)	0·0 to 2·0	99
Santa Cruz–Monterey area, California (confined aquifer)	0·0 to 1·3	97
Santa Cruz–Monterey area, California (water table overlying above confined aquifer)	0·2 to 6·3	97
Santa Clara River Valley, Ojai, Simi and San Fernando, California (32 wells)	0·1 to 1·3	100
Highland, California (1 well)	0·9	100
Southern Orange Co., California (7 wells)	0·4 to 1·0	100
Aberdeen (Owens Valley), California	9·3	100
Salton Sink area, California (5 wells)	0·2 to 3·9	100
Skull Valley, Utah	0·02 to 0·79	711
Hueco Bolson, N.W. of El Paso, Texas (94 wells)	0·0 to 0·49	81
Linn–Faysville area, Hidalgo Co., Texas (42 shallow wells)	0·8 to 36	98
Waikato district, New Zealand	0 to 28	65
Mikara City, Hiroshima, Japan	up to 2·8	67
Chambal, India	0·1 to 3	719
Patti, India	0·08 to 0·50	94
Intysh Artesian Basin, U.S.S.R.	0·07 to 0·83	91
Western Caucasus, U.S.S.R.	0·5 to 25	1042
Iraq	1 to 20	1073

amounts of boron on plant life. Thousands of well waters have been analyzed for boron content during the last thirty years, but potentially injurious concentrations have been found in relatively few, essentially confined to the 'boron belts' around the Pacific Ocean and across Eurasia.[823, 885, 1035] Other high-boron-content waters are from ancient brines or marine sediments[68, 716], or the displacement or squeezing out of interstitial waters during lithification.[91, 716] Most domestic and irrigation well water contains less than 0·5 p.p.m of boron, with much of it in the range of a few hundredths, of a p.p.m. A listing is given in Table XI of published well waters of higher than normal boron content; the water of some of these wells is useful only for supplemental water when rain is insufficient[81, 98], or for irrigating boron-tolerant crops. Additional information on the subject may be found in references.[89, 95, 101, 103, 708–11, 714, 715, 722, 723, 728, 729, 737, 1018, 1028]

Boron in Deep (Non-oilfield) Brines and Ground Brines

At a few places deeper wells have encountered saline waters not connected with petroleum deposits. These may be ancient (connate) brines resulting from the concentration of sea water, water in confined basins superimposed over older salt deposits, or synclinal brines whose salt content comes from the leaching of sediments. The boron content of these waters is high enough to be injurious to plant life, but the high salinity normally precludes their use for agriculture.[65, 98] A selection of typical published values is given in Table XII. Further data have been published in references.[713, 738, 1026]

Table XII.—Boron Content of Ground (Non-oilfield) Brines

Location of wells	Boron content, p.p.m.	Reference
Linn–Faysville area, Hidalgo Co., Texas (26 wells)	0·2 to 8·7	98
Cameron Co., Texas, near Brownsville (123 wells)	0·25 to 7·8	68
Salado, New Mexico	590	1126
Mojave Desert, California (23 wells)	0·1 to 35	1043
Aichi Prefecture, Japan	6 to 160	83
Chambal area, India	0·1 to 3	719
Turkmenia, Caucasus	3·4 to 128	255
Turkmenia	65 to 265	740
North Russian platform, U.S.S.R.	1·1 to 8·4	249
Cis-Carpathian District, U.S.S.R. (synclinal brines)	15 to 68	716
West-Caucasus Foreland, U.S.S.R.	1 to 270	1042
Western Cis-Caucasian Cretaceous, U.S.S.R.	8 to 25	724
Near Kirmakin Formation, Apsheron Peninsula, U.S.S.R.	87 to 219	252
24 Various Russian	0·9 to 13·3	246
Bulgaria	0·2 to 2,750	129

Boron in Oilfield Brines

Boron is found associated with oilfield brines throughout the world. These brines are either alkaline sodium bicarbonate type (Cenozoic), calcium chloride type (mostly Palaeozoic), or intermediate between these extremes.[249] Boron tends to accumulate in waters of a definite composition, being higher in the alkaline sodium bicarbonate types and lower in the calcium chloride types[232], where the high calcium content acts as a boron precipitant.[245, 1042] In many places the boron content increases with increasing salt content over the range of 0·5 to 25 g of total salt per litre, but decreases in stronger brines and highly saline waters. The boron content of oilfield brines also often increases with stratigraphic depth, but the total mineralization decreases with increasing depth.[229, 238] In some areas there is a positive correlation between the boron content and the carbon dioxide content of these waters, indicating a common or associated mode of entry into the water.[1042] Both hydrogen sulphide and carbon dioxide react with rock to liberate boron into the waters, especially at elevated temperatures and pressures.[236, 256] Most of the boron is genetically related to the alkaline constituents of the waters and to volcanic action during formation of the productive series.[228, 249, 260] The tectonic nature of an area greatly influences the boron content of the deep saline waters, higher boron concentrations occurring along deep faults and the associated fractured zones around faults and volcanoes, and in association with mud volcanoes.[228, 906, 1042] Where the carbon dioxide is thermometamorphic in origin, it acts vigorously to extract boron from rocks and aids its introduction into the waters of the fractured zones.[1042]

The boron content of these waters, along with the iodine, bromine and organic matter content, is an important aid in determining water genesis.[232] The accumulation of iodine, bromine and organic matter is less dependent on water type than is the accumulation of boron.[260] The boron, iodine and bromine concentrations in non-oilfield brines are controlled by the mineralogical and petrographical composition of the host rocks, the degree of formation sealing and the solubility of the com-

Table XIII.—The Boron Content of Oilfield Brines

Location	Boron content, p.p.m.	Reference
Baku, U.S.S.R. (alkaline Cenozoic)	4·0 to 198	249, 250
Baku, Urals, Dagestan (calcium chloride-saline)	6·7 to 140	249, 250
Azerbaijan (Apsheron Peninsula, U.S.S.R.)		
upper division	1·2 to 146	235, 260
lower division	62 to 233	
Azerbaijan (Baku, U.S.S.R.)		
Calcium chloride type waters	6 to 24	248
Transition from $CaCl_2$ to alkaline	82 to 117	
Alkaline	96 to 149	
Most alkaline (deepest)	184 to 231	
Bukhara-Khiva Region	27 to 57	257
Various Russian (alkaline bicarbonate)	200 to 1000	239
Russian Plateau	3·2 to 27·6	242
Shebalinka gas deposit	0 to 100	231
Bibi-Eibat	52 to 222	229
Surkhany	103 to 284	229
Sukhokumsk area, Dagestan (U.S.S.R.)		
sodium chloride-sulphate	42 to 161	993
Northern Dagestan (U.S.S.R.) 'Sheet Waters'	up to 430	991
Ural–Emba Interfluve (U.S.S.R.)	1 to 25	241
Timano–Pechor gas bearing basin	2·4 to 9·2	253
Volga–Ural gas field	28 to 56	253
Kuybyshev and Orenburg, U.S.S.R.		906
Devonian	5·6 to 12·4	
Carboniferous	15·5 to 31	
Permian (high Mg; low Ca, H_2S)	62 to 620	
Permian (high H_2S, sulphate; low Br, I)	18 to 39	
'Middle Asia'	40	907
Niigata City, Japan	7·6 to 9·1	254
Sodium chloride type waters:		1126
California	25 to 140	
Louisiana	20	
Hungary	5·4 to 89	
Japan	14	
Calcium-chloride-saline waters:		
California	trace to 8·3	
Louisiana	9·4	
Michigan	60 to 380	
Germany	0·8	
Sulphate-bicarbonate waters:		
California	3·9 to 13	
Wyoming	7·4 to 26	
Alberta, Canada	1·4	
Hungary	2·9	

ponents. In petroliferous horizons, these concentrations are additionally controlled by the distance from the sampling point to the oil–water interface.[234, 1017] The boron content of deep brines, when considered with the bromine, iodine and organic matter content, is an important indicator of the possible presence of petroleum in or near the area sampled.[127, 244, 258, 629, 630, 636, 641, 924, 991] The boron content of oilfield brines has been extensively studied in the Soviet Union. A selection of published data is given in Table XIII. Additional data on the subject may be found in references [237, 243, 247, 259, 618, 641, 715, 717, 718, 720, 724, 725, 908, 921, 1134].

Boron in Saline Lakes (Lakes of Internal Drainage)

Most fresh-water lakes are essentially wide places in rivers, and consequently only delay the flow of the water for a time on its way to the sea, perhaps effecting some concentration by evaporation or in some cases reduction in concentration of boron by adsorption by vegetable matter, especially under acid conditions.[734] Lakes of internal drainage, on the other hand, are for the most part terminal basins where the

Table XIV.—Boron in Saline Lakes

Name and location	Boron content, mg/litre	Reference
Large Soda Lake, Nevada	79	671, 672
Mono Lake, California	46	
Owens, Lake, California 1914	624	
Harney Lake, Oregon	268	
Big Lake, Wyoming*	298	
Track Lake, Wyoming*	246	
Red Lake, Wyoming*	148	
Lake Parinacochas, Peru	46	
Searles Lake, California, 135′ depth	7500	1043
Searles Lake, California, 90′ depth	3000	
Salton Sea, California	4 to 5	
Borax Lake, California	181 to 1077	
Alvord Borax Lake, Oregon	5	
Great Salt Lake, Utah	30	866
Brown Lake, California	470	294
Mono Lake, California	750	139
Soda Lake, California (normally dry)	666	139
Owens Lake sub-surface brine	540 to 3820	139, 1030
Various internal-drainage lakes, Western Victoria, Australia	0·1 to 28	732
Lake Urmia, Iran	5,000	885
Caspian Sea	1·5 to 3·2	255, 684
Aksukan Lake	135	255
Lake Inder, Kazakhstan	113 to 211	251, 575, 889
Black Sea	2·2 to 2·4	906
Aral Sea	2·1	
Kara Sea	3·6	
Lake El'ton	13 to 47	
Lake Aral-sor, Lake Tjube-sor	1·2	121, 122, 123, 124
Various lakes, Ural–Emba District	17·5 to 254	
Various inland saline lakes, U.S.S.R.	13 to 39	45
South-east Transbaikal, 32 lakes	over 1	135
South-east Transbaikal, 12 lakes	4 to 6	
Chokrak Salt Lake, U.S.S.R.	100	126
'Central Asia', many lakes	up to 745	136
Tbilisi	up to 48·6	119
Kulunda Steppe	0·06 to 60	131
Mangyshlak Peninsula	80 to 350	137
Western Kazakhstan	50 to 1100	120, 121, 122
Central Kazakhstan, 37 lakes	2·9 to 37	298
Central Kazakhstan, 6 areas	7·8 to 16·4	132, 138
Lake Sivash and Perekop Lake	11·5 to 173·5	44, 683

* Intermittent Lakes.

water evaporates more or less completely and the dissolved salts accumulate. Owing to the nature of the local climate, the brine level of these lakes fluctuates greatly; the lake sometimes dries up almost completely, at least on the surface, with the formation of a solid (often porous) salt bed, and at other times becomes considerably diluted. For this reason the reported constituent values vary widely for any given lake, depending upon the climatic conditions prevailing at the time of sampling and the depth at which the samples are taken.[140] A number of these lakes are, or could be, important sources of various salts for industry. A selection of published data on some of these lakes is presented in Table XIV. In general, the boron content is higher in alkaline lakes of the 'soda' (carbonate) type than in the sulphate and sulphate–chloride types.[131,133] All reported values have been converted to mg of boron per litre, since the various authors report the boron content in various ways.

The constancy of the ratio of boron to total salts noted for sea water is lacking for lake brines. This ratio is greater for fresh and brackish water than for brines, and all lake waters show a higher boron:chloride ratio than sea water.[66,133,135,298] Additional data are given in references [681] and [682].

Boron in Mud Volcanoes

The water associated with mud volcanoes in many parts of the world contains boron.[248,249,255,260,458,460,479,482,547,816,821,906,1042] These waters are predominantly of the alkaline sodium bicarbonate type[249], and originate in zones of young orogenesis, principally Cenozoic, but the source of some is older (Cretaceous).[248,260] Much of the original (at depth) alkalinity may be lost by mixing with intermediate-depth waters and reacting with the rocks through which the water passed on its way to the surface.[1042]

Mud volcanoes originate as a result of deep fissures where rising carbon-dioxide-rich waters leach boron from the host rock, and bring it to the surface.[981,1042] These waters are rich in boron and fluorine, resembling mineral springs in this respect, and are low in sulphate.[249] The presence of mud volcanoes is an indicator of nearby petroleum deposits[248]; the boron content of the mud volcano water ordinarily does not exceed that of the related oilfield brines of corresponding ages and districts. The boron content is higher in the chalk-volcanoes than in others.[240,479,906] A selection of published values is given in Table XV.

Table XV.—Boron Content of Mud Volcano Waters

Location	Boron content, p.p.m.	Reference
Kertch, Chalk volcanoes	47 to 1867	240
Georgia and Kertch	10 to 1600	248, 479
16 various Russian	average 175	249
Ak-Potlau	152	255
Lake Keimir	200 to 2,150	255
Lake Keimir borehole No. 2	76	255
Baku	31 to 139	255
Kertch	122 to 1764	448, 460
Odessa	0·8	448
Georgia	2	448
Sormat, Produktivnaya, Shirakan thickets	under 3	479
Georgia ($CaCl_2$ type, Kilakupra)	74 to 85	816
Kertch, Taman, Apsheron	102 to 2150	906

Commercially valuable boron deposits have been formed by accumulation of borates in areas adjacent to mud volcanoes.[448,456,458,482,821,885] Prior to the discovery of the Inder deposits in Kazakhstan, the mud-volcano borate deposits of the Kertch Peninsula were the only practical borate source in the Soviet Union, borax being extracted from muds ranging in content from 0·3 to 0·4% B_2O_3, equivalent to 0·09 to 0·12% boron.[456,457] The $Na_2B_4O_7$ content ranges up to about 42% of the total salts present in the dried-up accumulations around the mud volcanoes.[448] These are not now being utilized.

Boron in Volcanic Emanations

In addition to the thermal springs, geysers and soffioni, there are many places where gases escape from volcanic vents. These gases are usually acidic, hot and contain much water vapour and at places much native sulphur. Other gaseous components include hydrogen, helium, neon, xenon, nitrogen, ammonia, hydrogen chloride, hydrogen fluoride, carbon monoxide, carbon dioxide, carbonyl sulphide, hydrogen sulphide, sulphur dioxide, arsenic and at times a considerable amount of boron in the form of sassolite.[449, 452–4, 464–8, 473–5, 814, 815, 817, 824, 1128] The composition of the gas changes with decreasing temperature during a single eruptive cycle, the boron content becoming less as the temperature decreases.[465, 474, 475] A few vents have yielded the fluoborates avogadrite and ferruccite.[476, 480] Few of these vents have accumulated substantial borate deposits, but over millions of years their collective contributions of boron to the atmosphere must have been enormous.[463, 471, 473, 475, 817] The boron content of the condensate from several fumaroles is given in Table XVI.

Table XVI.—Boron in Fumarole Condensates

Date	Location	Boron content, mg/litre H_2O	Reference
2 Sept. 1953	Kamchatka (Central Crater No. 1)	1·7	1128
13 Dec. 1953	Kamchatka (Central Crater No. 1)	1·1	
2 Sept. 1953	Kamchatka (Seulich Dome)	0·8	
10 Aug. 1952	Hekla (Shoulder Crater)	4·1	
1932	Santa Maria	1·6	
1939	Seven Dwarfs B/1	129	
1939	Seven Dwarfs A/5	46	
1939	Seven Dwarfs A/6	33	
1939	Seven Dwarfs B/20	86	
1939	Seven Dwarfs B/22	32	
—	Kilauea Iki, Hawaii	0·6	
Sept. 1954	Showa-Shinzen, Hokkaido, Japan, A-1 (9081)	39*	
1954	Showa-Shinzen, Hokkaido, Japan, A-3 (9051)	21*	
1954	Showa-Shinzen, Hokkaido, Japan, C-3 (9063)	5·6*	
1962	Avachinsk	13·4–73	465
1953–1957	Suclich	141–1130	474

* p.p.m. by weight.

BORON IN THE LITHOSPHERE

The lithosphere is the solid portion of the earth's surface, excluding ice, and it includes the submerged solid crust as well as the exposed areas.[63, 660, 662, 1009] Generally, it is considered to average ten miles in thickness, although there are differences of interpretation among authorities and there are great variations in thickness from place to place. Under the high mountain ranges it is thickest, and in the deep sea trenches it is thinnest.[660]

For simplicity of treatment, the lithosphere is here divided into three major divisions: igneous, sedimentary and metamorphic rocks, with some latitude as to placement. The major divisions are further subdivided where there are great differences in boron content.

Since about 1950, there has been a great increase in interest in the boron content of all parts of the earth; the literature is voluminous.

Boron in Igneous Rocks

As used here, 'igneous' rocks includes the rocks of indisputable igneous origin, such as the rhyolitic, basaltic and ultra-basic rocks, as well as the granitic and syenitic rocks, some of which may be of questionable igneous origin.

Igneous rocks are in general lower in boron content than sedimentary rocks[662], and the boron content of igneous rocks increases with the acidity of the rocks from ultrabasic to acidic[648,1019], but there are exceptions.[850,851,992] Boron is a highly mobile element, so variables such as temperature, pressure, rate of cooling, initial water content, rock composition, sequence of events, etc., greatly influence the proportion of original boron retained upon cooling.[841] Boron is present in magmas as the B^{3+} ion in two distinct configurations. When it occurs as the centres of BO_3^{-3} triangles it is not readily accepted into the lattice of silicate minerals (because of geometry problems), so it forms borate or borosilicate minerals, with most of the boron accumulating in the residual melt, and ending up in a pegmatite or endogenetic deposit. The boron which is present as the centres of BO_4^{-5} tetrahedra, on the other hand, is preferentially incorporated into many silicate minerals.[838] Plagioclase is the principal collector of boron in igneous rocks[358,515,543,841,851,914], although hornblende also acts as a boron collector.[492] Higher boron content is typical of the well-crystallized granitic–syenitic rocks, and a lower content is typical of the less well-crystallized aplites, granitic porphyries, and leucocratic granites, which apparently crystallized with an intense removal of volatiles.[841] The lower boron content of some lavas and subvolcanic mafic rocks may be due to the initially higher water content of the magma, with separation and solution of some of the boron during cooling and solidification.[850] Eruptive rocks are generally higher in boron content than their corresponding intrusives[881], especially submarine eruptives, which often are enriched in boron.[851] Volcanogenetic rocks of an initial eruption are often richer in boron than those of later stages.[487] Quiet, fissure-type eruptions produce rocks of a higher boron content than products of explosive eruptions, owing to loss of boron as a part of the volatiles during violent eruptions.[851] The highest boron content is found in intrusive massifs of Devonian age.[843] By reaction at the boundary of ultra-basic deep-seated (intrusive) rocks with sediments or their metamorphic successors, boron can increase in the adjoining rock. Borosilicate crystallization is possible at these contacts.[330]

The great mobility of boron makes it difficult to obtain a truly representative sample of a rock formation, as the boron content is often quite different in the interior of a mass from the value at the surface.[1019] Local areas such as pegmatites may be boron-enriched at the expense of the bulk of the rock mass.[63,493,500,530,838]

Many values are reported in the literature which are considerably higher than the generally accepted world-wide average boron-content values of particular rock types. It is very probable that many of these published values represent the exception rather than the rule, and were investigated at least partly because of their higher-than-normal boron content and may, therefore, be considered to be atypical.

Table XVII gives recently published values for the boron content of rocks divided roughly into three groups according to their acidity. This arbitrary division is only approximate, as many authors classify the rock types by different systems.

The literature concerning boron in igneous rocks is voluminous. Some additional references include for eruptive rocks: [267,289,450,469,477,481,483,497,776,818,822]. For intrusive rocks: [496,498,502–7,511,512,514,516–21,527–9,531–4,536,537,544–9,551,774,775,830–2,834,836,840,844,846,847,849,855–7,970,977,980,983,1001,1004,1024,1075].

Pegmatites, being the last portion of a granitic intrusion to solidify, contain a concentration of the scarcer elements originally present in the intrusive mass; thus the pegmatite is notably enriched in these elements, including boron.

Presumably in most instances the greater portion of the boron was present in the original magma, but some pegmatites seem to have acquired additional boron by solution or absorption from sediments through which the magma intruded.[544] Some of the usually boron-barren minerals, such as cookeite, formed during solidification of a boron-rich pegmatite, include boron in their crystal lattice when crystallizing from such a melt[1149], but the bulk of the boron forms characteristic borosilicate and anhydrous borate 'pegmatite minerals'. By far the greatest of these, in both quantity and diversity of composition, are the ever-present tourmalines, individual crystals of which sometimes reach enormous size.[1175] In some pegmatites tourmaline is the

Table XVII.—Boron in Igneous Rocks

Location	Boron content, p.p.m.			Reference
	Mafic	Intermediate	Acidic	
Worldwide	1·5 average		3 average	662
Worldwide	2·5 to 60 average 6	5 to 20 average 13	25 to 60 average 30	495
Worldwide	average 5	average 10	average 30	493
Worldwide, earthcrust average	3 to 5		9 to 10	1019
Worldwide			average 15	1039
Worldwide	1·5 to 3		3	669
Connecticut, U.S.A.	13 to 2360			499
Connecticut, U.S.A.	50 to 450			494
New York, U.S.A.	3 to 920			539
Nevada, U.S.A.		100		1039
California, U.S.A.			10 to 50	488
New Zealand	12 average	28	25 average	825
Japan	4 to 10			484
Japan (most)			6 to 8	484
Japan, Kitalami district			average 34	484
India			63	508, 853
Sweden (Vätö)		10		510
Thuringian Forest			55 to 122	914
Pantelleria and Sardinia		10 to 80		1039
Italy	42 to 135		77 to 205	486
Elba and Giglio Islands			5 to 276 average 50	547
Romania	950	10 to 30	10 to 1060	881
Hungary			6 to 16	973
Czechoslovakia (Ransko)	0 to 20	29 to 120		982
South Africa			average 50	541
Russia and others			50 to 200	492
Urals	20 to 30		12 to 30	833
Urals	0 to 40	0 to 150	0 to 80	535
Orenburg region, U.S.S.R.	0 to 130			542
Khanka Lake region, U.S.S.R.			620	523
Burpala Massif, U.S.S.R.			5 to 180, average 14	854
Eastern Sayan			0 to 95	509
SW offshoots of Gissar Range, U.S.S.R.				851
(basalt)	600	2400	1700	
(tuffs)	600	1900	1100	
Chukota			120 to 320	657
Kunashir Island		21	42	1135
Miao-Chang (Khabarovsk)			40 to 600	501, 524 525
Eastern Kazakhstan (Kalba)			0 to 31	522
Lovozero Massif, U.S.S.R.		1 to 38		538
Bitu-Djinsk Massif, U.S.S.R. (S.W. Cis-baikal)			22 to 39	845
El'dzhurton (Mesozoic)			1 to 3	551
Kurarna Ridge, U.S.S.R.			31	827
Gornyi Altai, Siberia	15 to 40		120 to 880	487
Western Tien-Shan		5 to 66		489
Tien-Shan	1 to 38			850
Western Siberia	4 to 8	10 to 14	1 to 12	992
N.E. U.S.S.R. (tin-bearing)			230	550
So. Yakutia			below 20	543

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only boron-bearing mineral present. Pegmatites are known from many regions of the earth, where there have been granitic intrusions. Listed in Table XVIII are some of the published occurrences of boron minerals in pegmatites.

Table XVIII.—Boron Pegmatitic Minerals

Mineral	Reference
Behierite	1161
Cappelenite*	1171
Caryocerite*	1169, 1171
Dumortierite*	1153, 1158, 1160, 1168
Gadolinite*	834, 840, 1154, 1117
Grandidierite*	840, 1117, 1153, 1167
Hambergite	1165, 1172, 1173
Hellandite*	834, 1163
Kornerupine*	1166
Leucosphenite*	1155
Manandonite*	1159
Melanocerite*	1164
Nordenskiöldine	1172
Rhodizite	1157
Spencite*	1156, 1170
Stillwellite*	1150, 1162
Tadzhikite*	1152
Tienshanite*	1151
Tritomite*	1156
Tourmaline*	530, 544, 1174–95

* Borosilicates.

Boron in Sedimentary Rocks

There has been a large investigative effort in recent years concerning the boron content of sedimentary rocks, due largely to the possibility of determining the environmental conditions of the ancient seas or lakes in which the sediments were laid down. Much of this interest is due to the role of boron in mineralization (see Boron in Petroleum and Concentration of Boron sections).

Goldschmidt and Peters in 1932 determined the boron content of a number of rock types, and first recognized the increased boron content of argillaceous marine sediments.[669] Landergren in 1945, 1958 and 1964 studied the boron content of some Swedish and Atlantic sediments and elaborated on the work begun by Goldschmidt and Peters, and established the fact that the boron content of these sediments was related to the salinity of the water at the time of deposition as determined by the fossil fauna[271, 273, 754, 1036], and to some extent to the grain size of the sediments. In 1960, Frederickson and Reynolds[263] determined that the fine clay fraction of sediments contains the bulk of the boron, and while the chlorite, kaolinite and illite components of this fine clay fraction all adsorb boron from sea water, the illite fraction is by far the most significant, and can be used to estimate the paleosalinity with a reasonable degree of accuracy.

The above works were summarized and elaborated upon by Harder in 1963.[277] Several additional parameters were introduced by him, including residence time, rate of deposition, temperature, distance from source to point of deposition, particle size, mineral composition of the sediments, etc. Many other researchers have followed up the clues provided by the above workers, and a voluminous literature on the subject has appeared.

A few researchers dispute the validity of the boron method of estimating palæosalinity of sediments[280, 766, 770, 972, 1037], but most accept it with limitations or variations. Some consider the whole-rock boron content the most important[269, 279, 284, 306, 757, 767]; some consider the whole clay fraction the most important.[309, 766, 882, 941, 1014] Some consider particle size of prime importance[265, 266, 271, 309, 312, 765, 768, 851], while other (non-illite) clays are considered to be important by others.[264, 747, 749, 768,

[1037] Organic carbon has been reported both to increase the boron content[282,306,765,1012] and to decrease the boron content by acting as a diluent.[917] Other authors have reported on the dilution factor[747,765] as being of prime importance, whereas still others consider climatic conditions at the time of deposition to be of great significance.[748,764,1023] The sedimentation rate[277,749,765], pH[747], time in contact with the water[748] and original boron sources[1036] have also been discussed. The effect of the presence of other non-clay boron-bearing minerals such as tourmaline[266,285,765], feldspars[917], muscovite[759] and recycled illite[318] has also been investigated.

As a result of their work published in 1960, Frederickson and Reynolds developed the concept of 'normalized boron', actually the boron content of the illite fraction of a sediment, utilizing X-ray fluorescence techniques, for determing palæosalinity.[263] Later refinements of this technique include Walker's 'adjusted boron' concept[285,917]; his departure curves[265], and 'equivalent boron'[282]; Frederickson's 'partition coefficient'[303]; and Curtis's B/K ratio.[306] These are all improvements on the original concept, but may not be sufficient alone to determine palæosalinity with certainty.[972,1037] Potter *et al.*[305] have introduced the 'discriminate' concept, using statistical methods wherein equations have been developed covering marine and non-marine argillaceous sediments, both modern and ancient, utilizing as variables contents of six trace-elements (boron, chromium, copper, gallium, nickel and vanadium). However, the most efficient discriminant function was based on the boron and vanadium contents alone; 28 out of 33 ancient shales, whose depositional environment was known, were correctly classified.

The boron content of carbonate and sulphate sediments (limestone, dolomite, magnesite, siderite, gypsum, anhydrite) presents a special case. Goldschmidt determined that the boron content of carbonate sediments was low, about 10 p.p.m.[662], which has since been confirmed by a number of investigators.[268,279,296,768,829,851,1019] More recently it has been determined that in the normal marine carbonate sediments the boron is largely contained in the included clay fraction[277,969,1014]; therefore, the boron analytical values for the whole rock sample must be corrected for the carbonate content in order to correct for dilution.[765]

Under suitable conditions, i.e. when the water contains from 0·5 to 1·0% of B_2O_3, the BO_3^{3-} ion can isomorphously replace the carbonate ion in carbonates such as limestone and dolomite, and the sulphate ion in sulphates such as anhydrite; high ambient temperatures and an arid climate apparently promote this replacement.[1023]

Experiments have shown that boron is adsorbed by clay minerals, particularly illite, in proportion to the salinity of the solution (borate ionization increases with increasing salinity), and also in proportion to the boron concentration in the solution, over the expected concentration range of natural (fresh to sea) waters. This sorption is independent of the original boron concentration of the illite, and all illites do not behave in the same way[281,747,749,756], but they are more nearly alike when reduced to an equal surface-area basis.[839] Time, temperature and particle size are all contributing factors. The available data seem to fit the Freundlich adsorption isotherm quite well; one form of this equation is

$$\log (x/m) = \log a + b \log c,$$

where x/m = moles sorbed per unit mass of sorbent, c = equilibrium molar concentration of sorbate in solution, and a and b are empirical constants which vary according to the particular clay fraction involved.[756,839]

There seems to be more than one mechanism for incorporation of boron into the clays: (i) a rapid adsorption of the $B(OH)_4^-$ ion at the tetrahedral sites at the 'frayed edges' of the clay flakes, with a weak ionic bond and an epitaxial fit due to the tetrahedral geometry of the units there, and (ii) the migration of the chemisorbed $B(OH)_4^-$ ions through the structure by the formation of Frenkel and Schottky crystal defects[742,744,839], where the boron proxies for silicon or aluminium at the tetrahedral or octahedral sites.[287,749,839] The maximum experimental uptake of boron by illite seems to be about one borate ion per 100 square ångstroms, consistent with a

Table XIX.—Boron in Argillaceous Sediments

Location	Boron content, p.p.m.			Reference
	Marine	Brackish	Non-marine	
Modern Pacific Pelagic Sediments	96–490			287
Mean	300			
Pacific Ocean	37–193			754
Mean	134			
Indian Ocean	43–183			
Mean	115			
Atlantic Ocean	93–192			
Mean	131			
Tyrrhenian Sea	96–227			
Mean	143			
Pennsylvania	50–160	35–140	15–110	275
Mean	115	92	44	
Colorado	99–297	122–237	50–120	747
Modern Gulf of Mexico, South Pacific, various interior U.S.	51–121		10–99	305
Mean	90		46	
Ancient, various U.S.	32–178		8–83	
Mean	124		40	
North and South America, Pacific Ocean	38–183		12–159	882
Mean	105		58	
Western Interior U.S.				268
Non-carbonaceous			30–130	
Mean			78	
Carbonaceous			50–160	
Mean			99	
Near Shore	60–160			
Mean	112			
Off Shore	40–220			
Mean	130			
North American Black Shales	<20–>200			770
Illinois (Pennsylvanian)	130			829
Southern Appalachians, U.S.A. Cretaceous	45–140		23–36	756
Finland Pre-Cambrian	130–220		10–160	755
Mean	160		45	
Finland	30–3000			301
Germany	82		15–146	279 302
Germany	330	240		284
Germany		80–100		311
Worldwide	100			1019
Koster, Bohuslän	140			1036
Allsbäck, Gullmarsfjord, Bohuslän	100			
Gulf of Bothnia		30		
S.W. Spurs Gissar Range, Central Asia	60	160	29–74	293 851
Transbaikal	129		32	910
Central Asia (Tien-Shan)	36–113	74	52–119	266 768
Russia (present-day silts):				313
Northern Inland Seas	29–107			
Southern Inland Seas	52–62			
New Zealand			20–60	757
Japan			0·6–8·6	270
Baltic Sea	20–180			1125
Black Sea	15–200			
Mediterranean Sea	15–300			
Atlantic Ocean	25–300			
Lagoon of Santorin Volcano (Iron-ore sediment)	2600–6400			

monolayer limit to the adsorption.[839] In time some of the adsorbed boron becomes immobilized by becoming incorporated into authigenic tourmaline.[662]

A selection of published values for boron in argillaceous sediments is given in Table XIX, for arenaceous sediments in Table XX and for carbonate sediments in Table XXI.

Table XX.—Boron in Arenaceous Sediments

Location	Boron content, p.p.m.	Reference
Europe, North and South America	5–10	662
Worldwide	35	1019
New Zealand (greywacke)	20–33	757
Central Asia (sandstone)	43	768
Crimean Mountains (sandstone)	30–370	289
Tien-Shan	25	266
South-west Spurs of Gissar Range, Asia:		
Conglomerates and gritstone	9–14	851
Sandstone	26–62	
Colorado Plateau Sandstone	16	1123

Table XXI.—Boron in Carbonate Sediments

Location	Boron content, p.p.m.	Reference
Worldwide	1·5–3	662
Worldwide	20	1019
Illinois (Pennsylvanian)	18	829
Eastern Kansas	0·5–300	322
Mean	21	
North America, Europe, Africa:		1014
Dolostones	13–340	
Mean	68	
Dolomites	49–340	
Mean	144	
Western Pennsylvania, clay fraction only:		276
Marine	133–1200	
Non-Marine	40–90	
Westphalia	70–800	297
Germany	3–50	279
Mean	15	
South-west Spurs of Gissar Range, Asia	41–76	851
Crimean Mountains	11–750	289

Additional references concerning boron and palæosalinity include: [261, 291, 292, 300, 304, 308, 617, 751, 756, 976, 1007, 1009, 1016, 1117, 1121].

Additional references concerning boron in marine sediments include the following: [262, 278, 281, 283, 310, 320, 321, 648, 741, 743, 745, 752, 758, 762, 970, 1000, 1010, 1022, 1118, 1120, 1122, 1124].

Aditional references concerning boron in non-marine sediments include: [316, 750, 753, 760, 777, 968, 974, 994, 1003, 1008, 1011, 1015].

Additional references concerning boron in carbonate sediments are: [315, 896, 1119].

Boron in Pore Waters

Data on the interstitial or pore water of sediments are scarce. Available analyses of this pore water indicate that at least in the Pacific Ocean, and in some closed-basin lakes of the sodium chloride–alkaline type, where the organic carbon is high, the boron is largely retained and the chloride largely expelled during compaction.[274, 287, 298] This gives a two- to five-fold increase in the boron content of the pore water as compared to the original lake or ocean brine, and a corresponding ten- to hundred-fold increase in the boron:chloride ratio.[57, 286] In sediments of low organic carbon content where brines are of the sodium–calcium chloride type, boron impoverishment of the pore waters sometimes occurs.[274] In fresh-water lake sediments there does not seem to be any correlation between the organic carbon and boron contents.[298]

A selection of published values is given in Table XXII.

Table XXII.—Boron Content of Pore Water in Sediments

Location, sediment type	Boron content, p.p.m.			Reference
	Lake brine	Pore solution	Bottom mud	
Pacific Ocean, Pelagic	4·6	11–22		287
Mean		17		
Pacific Ocean, Red Clay	4·6	5·2–7·6	46–99	274, 680
Mean		6·3	84	
Pacific Ocean, Diatomaceous Mud		3·8–5·0	85–110	
Mean		4·4	101	
Pacific Ocean, Globigerina Ooze		4·2–5·2	28–31	
Mean		4·7	29	
Pacific Ocean, Calcareous Mud		6·0–6·7	38–42	
Mean		6·2	40	
Gulf of Mexico	4·6	2–12		659
Black Sea	4·6			228, 274, 680
(a) Chloride-alkaline waters:				
Clay mud, recent		2·4–4·5	93–98	
Clay mud, ancient		2·6–3·8		
Clay mud, New Euxinian		3·3	73–81	
Mean		3·4	87	
(b) Chloride-sodium-calcium waters:				
Clay mud, New Euxinian		0·2–2·4	64–71	
Mean		1·3	67	
Central Kazakhstan:				
Salt Lakes	2·8–37	3·0–29	3·6–66	298
Mean	11	12	27	
Fresh-water Lakes	0·33–0·36	0·38–0·87	3·7–9·8	
Mean	0·34	0·66	6·1	

Boron in Metamorphic Rocks*

Metamorphic rocks are produced by the mineralogical and structural adjustment of solid rocks to physical and chemical processes operating at depth below the zone of weathering, and differing from those processes under which the original rocks were formed.[660, 1314] Details of the formation and classification of such rocks are complex and will not be discussed here; interested readers may consult selected references concerning metamorphism and its geochemistry.[660, 1234, 1308–14, 1411, 1412] Published information on boron in metamorphic rocks is voluminous but widely scattered; only some of the pertinent references can be cited below. One of the more important of these is the monographic study of Aleksandrov, Barsukov and Shcherbina[1199] on the geochemistry of boron in endogenetic processes (including those of contact metamorphism).

The geochemistry of boron in metamorphic rocks is not as well known as that of boron in magmatic and sedimentary rocks, despite an abundance of published observations, chiefly because of the complex origin of such rocks. In general, the content of boron in metamorphic rocks is intermediate between that of sedimentary and igneous rocks.[444, 495, 1416] As in the igneous rocks, the coordination of the boron atom plays an important part in its geochemical behaviour in metamorphic rocks. The common rock-forming silicates show little affinity for boron, especially in three-fold coordination.[838] In borosilicates, boron is known in three-fold coordination in only four minerals: dumortierite[1259, 1260, 1262], grandidierite[1167, 1260, 1262, 1372], harkerite[1262, 1401] and tourmaline[1260–62, 1371]; in both three- and four-fold coordination in garrelsite[1256] and howlite[1258]; and in four-fold coordination in all others. Christ[1336] suggests that SiO_4 tetrahedra in silicates are replaced by $BO_3(OH)$ tetrahedra, but that under some conditions boron may proxy for tetrahedral aluminium, especially in the more disordered structures. Such substitution is only partial, however, in natural minerals.[1338, 1340]

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* This section on boron in metamorphic rocks is by R. C. Erd, the author also of the previous main section (A1) on Boron Minerals.

Table XXIII lists the boron content of some minerals in metamorphic rocks; data for this compilation were included only for those minerals stated specifically to occur in metamorphic rocks. These data are less often reported than for the same minerals occurring in igneous rocks, since metamorphic rocks are more difficult to separate into their constituent minerals. Some data[495] appear to be more reliable than others, in that the presence or absence of intergrown or included boron minerals or fluid inclusions containing boron in solution[1366] have been considered. Harder[495] suggests, for example, that the high-boron andradite of Bertolani[1253] may have been intergrown with a boron mineral. Getling and Savinova[343] have shown that wollastonite, with an apparent high boron content, actually contained microscopic crystals of datolite which had even partly replaced the wollastonite. However, they state that a high-boron (1000 p.p.m. boron) garnet, comparable with the value given by Bertolani, contained no contaminating boron mineral. The boron content may vary considerably within a single specimen or even within a single crystal, as in zoned idocrase.[342, 1327]

Table XXIII.—Boron Content of Some Minerals in Metamorphic Rocks

Mineral	Boron content, p.p.m., Range	No. of determinations	Reference
Graphite	86		1325
Quartz	0–30	3	514
	1	1	914
	16	1	342
	0	1	495
Pyrope	2	1	495
Almandine	2–9	4	495
	0	1	1253
Grossular	0–<9	2	1253
Andradite	1–3	3	495
	0–3913	5	1253
Garnet	21–100	25	342
	0–1000	18	343
	400	(‘average’)	514
	100	1	1324
Garnet (in eclogite)	3–5	50	1001
	21–41	11	1301
Sillimanite	<9	1	1253
	140–360	4	1254
Andalusite	0–8	3	495
	<9	2	1253
	<20	4	1254
Kyanite	0	3	495
	0–<9	2	1253
Staurolite	5	1	495
	0	1	1253
Sapphirine	2329	1	1415
	495	1	1186
	200	1	1324
	0	2	1332
Norbergite	60	(Maximum value)	1255
Chondrodite	155	(Maximum value)	1255
Humite	310	(Maximum value)	1255

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Table XXIII.—(continued)

Mineral	Boron content, p.p.m., Range	No. of determinations	Reference
Clinohumite	310	(Maximum value)	1255
	2516	1	1331
Sphene	70	1	342
	1	1	495
Chloritoid	0	2	1253
Gehlenite	0	1	1253
Epidote	22–330	14	342
	0–30	9	343
	0–3	6	495
	<9–53	5	1253
Piemontite	1	1	495
Zoisite	1	2	495
	0	1	1253
Idocrase	230–12,500	4	342
	3–180	3	495
	6211	(Maximum value)	860
	<9–1127	3	1253
	1242–3727	(Zoned specimen)	1327
	186	1	1328
	31–2112	2	1329
	600	1	1330
	186–2516	3	1331
	0–7764	19	1333
Cordierite	1–4	2	495
	<9–9	2	1253
	155	(Maximum value)	1255
	150	1	1324
Diopside	5–300	7	357
	2	1	495
	0–<9	6	1253
Hedenbergite	<9	1	1253
Jadeite	<9	1	1253
	20	1	1322
Omphacite	3–6	36	1001
Hypersthene	150–880	3	357
	100	1	1324
Pyroxene	8–89	38	1208
Tremolite	220	1	490
	2	2	495
	0	1	1253
Hornblende	30–300	6	357
	0–100	3	514
	7	1	914
	0–<9	4	1253
	28–56	10	1319
Hornblende (Karinthine)	20	2	1001
Glaucophane	6–10	2	495
Amphibole	19–29	5	1208
Wollastonite	10–200	8	343
	0	1	1253
Prehnite	1	1	495
	13,400	(Maximum value)	860
	0–916	9	1253
Apophyllite	6	2	495
	1304	1	780
Pyrophyllite	0–6	5	495
Talc	2	1	495
Paragonite	70–210	7	495
Muscovite	11–1480	13	495
	55–100	4	914
Phlogopite	32	1	495

Table XXIII.—(continued)

Mineral	Boron content, p.p.m., Range	No. of determinations	Reference
Biotite	2	1	342
	2–8	2	495
	0	3	515
	5–15	7	914
	28–53	10	1319
	30	1	1324
Clinochlore	6	1	495
Chlorite	18–90	3	342
Antigorite	25	1	495
	10	1	1323
Lizardite	13	1	1323
	13–65	2	1327
Chrysotile	750–930	3	490
	15	2	495
	16–33	4	1323
Serpentine	100	1	342
	15–160	2	495
Potassium feldspar	30	3	514
	5	1	914
Plagioclase	10–200	9	343
	100–160	3	514
	100	1	914
Scapolite	13–39	3	495
	<3–214	2	1253

While boron content may be low or absent in the natural mineral in metamorphic (and igneous) rocks, boron analogues of some of these minerals have been synthesized: gehlenite[1334], muscovite (partial substitution)[1338], phlogopite[1335, 1338, 1339, 1341], potassium feldspar[1337, 1338, 1340] and albite (synthetic reedmergnerite).[1337] Borosilicate minerals (not listed in Table XXIII), especially tourmaline, concentrate most of the boron present in metamorphic rocks. Since tourmaline may make up as much as 90–95% of some schists[1271], boron content may therefore have a possible range from a maximum of about 10% of B_2O_3 (or about 31,000 p.p.m. boron) to essentially nil in the highest-grade metamorphic facies. In actuality the normal range is close to that shown by Harder[444]: a maximum of 1860 p.p.m. boron in a kyanite–mica schist to a low value of a few p.p.m. boron (nil in some cases) in eclogites and granulites. Because of the variability of the boron content in metamorphic rocks it is impracticable to tabulate such data here. Published values for boron in metamorphic rocks are numerous; see selected references.[295, 320, 323, 325, 339, 444, 513, 534, 535, 542, 543, 648, 742, 755, 781, 785, 790, 835, 851, 914, 1001, 1056, 1199, 1206, 1282–84, 1301, 1322, 1323, 1365, 1374–85, 1408]

The source of boron in metamorphic rocks has been a matter of some dispute. Examples of isochemical metamorphism, with the source of boron arising from the metamorphosed sediments themselves, are cited by many authors.[299, 338, 543, 544, 648, 669, 790, 851, 881, 942, 1217, 1231, 1238, 1271, 1272, 1274, 1281, 1284, 1286, 1365, 1368, 1380, 1382–93, 1398] In contrast, allochemical metamorphism (metasomatism), or a source of boron from within an intruding magma and supplied to the metamorphosed rocks, is favoured by others.[335, 336, 340, 881, 1248, 1276, 1310, 1395–7, 1399] A few workers have stated that the source of the boron cannot be decided for a particular occurrence in metamorphic rocks.[535, 815, 1218, 1394] In a few instances the same rocks have been studied with exactly opposite opinions as to the origin of the boron present. Thus, Darnley[1397] claimed that boron in the metamorphosed Katanga metasediments of the Rhodesian Copperbelt was added from a magmatic source, whereas Mendelsohn[1398] favoured a sedimentary origin. Similarly, Shabynin[336, 1248] argued for a metasomatic origin of boron in the metamorphosed iron ore deposits of the Aldan shield in southern

Yakutia rather than the sedimentary source postulated by Serdyuchenko[288, 338, 350] and by Egorov.[543] In general, the preponderance of recent studies seems to favour the remobilization of boron from sedimentary country rocks in regional metamorphism (see below) and in some instances in contact metamorphism.[1231, 1238] However, there is evidence that both processes may be operative[1199], with the intrusive magma representing a source of boron supplementary to that already present in the metamorphosed sediments. The source of boron may arise through the absorption of aqueous solutions at depths from the country rocks and by a re-transfer of boron to the metamorphosed rocks at shallow depths (less than 6 km), according to Barsukov.[1199]

Boron content may be useful in determining whether metamorphic rocks were derived from an igneous or sedimentary parent rock. Several studies have shown that paragneisses (formed from pre-existing sediments) have higher boron contents than do orthogneisses.[444, 914] Lyakhovich[1400] notes that the primary sedimentary nature of paragneisses can be determined from the composition of the accessory minerals, citing, among other criteria, the high magnesium content of tourmaline found in such rocks. Granites formed by ultrametamorphism, or partial to complete fusion, of sedimentary rocks appear to be enriched in boron in comparison with their magmatic equivalents.[541] Such enrichment of boron, however, may also be due to extreme fractionation rather than to a sedimentary origin; such fractionation may be recognizable from the concomitant concentration of elements such as rubidium, cæsium and thallium with boron.[1414] More importantly, boron follows the course of potassium and fluorine in the fractionation of magmatic materials[547, 1199] and typically accompanies these elements in both regional and contact metasomatism.[774] Tourmaline with a relatively high content of fluorine is probably indicative of a magmatic rather than a metamorphic (or sedimentary) origin.[1402–7]

In further discussion of the geochemistry of boron in metamorphic rocks it is convenient to consider the behaviour of boron in the broad divisions of regional and contact metamorphic processes.

(I) BORON IN REGIONAL METAMORPHISM

Modern ideas on the geochemistry of boron in regional metamorphism began about forty years ago when Goldschmidt and Peters[669] noted that the boron content of marine clays and shales could adequately account for the boron values of their metamorphosed equivalents without the necessity of externally introduced (metasomatic) boron. Many studies since that time have shown that the greatest concentration of boron in sedimentary rocks is in the illitic fraction of marine clays (see Boron in Sedimentary Rocks, above, and references).[755, 756, 1209, 1212, 1285, 1315, 1316] It has been estimated[678] that about $3{\cdot}3 \times 10^8$ kg of boron are removed annually from the ocean in this manner—about five times as much boron as is removed by all other processes. Mixed-layer illite/montmorillonite may also contain appreciable boron, while chlorite and muscovite contain only minor amounts.[235, 495, 1209] According to Harder[1209] the uptake of boron by illite occurs in two steps; first, by surface adsorption of boron and, second, by incorporation into the tetrahedral sites of the mica structure. The first process is rapid; the second a very slow surface reaction which, however, proceeds more rapidly as the temperature is elevated. The charge of the boron atom and its size make it probable that boron replaces aluminium in the highly accessible outer tetrahedral positions. Surface adsorption has been shown to increase with reduced crystallinity in some experiments on grinding and heating.[1214] Well-crystallized muscovite in sediments has a much lower content of boron than illite.

Several recent studies[1212, 1251, 1252, 1257] have been made of the diagenesis of marine pelitic sediments. Briefly, transformations are from montmorillonite to mixed layer illite/chlorite/montmorillonite during burial diagenesis and from mixed-layer illite/montmorillonite to muscovite and chlorite during the early stages of regional metamorphism. During diagenesis boron continues to diffuse into the illite structure, the process being accelerated both by higher temperatures and by greater concentration of pore fluids. The polymorphic transformation of the 1*M* disordered illite into 2*M* muscovite, accompanying early stages of metamorphism, involves the expulsion of boron from the mica structure. Muffler and White[1257] have found this transition to occur at temperatures below 210°C in the Salton Sea geothermal field.

There is a continuous spectrum between diagenesis and metamorphism and, with rising temperature, the greenschist facies appears at about 300°C.[1317] In this facies the dioctahedral mica, muscovite, appears to be exclusively the 2*M* polymorph. The appearance of the greenschist facies thus marks the redistribution of boron[1321] and much of the original content of the sediment may be lost to the hydrologic cycle at this point, accompanying other mobile components. However, much of the boron thus released may become fixed by the formation of tourmaline[1321], which makes its first appearance in the lower greenschist facies. Tourmaline is the most abundant and important boron-bearing mineral in regionally metamorphosed rocks.

Goldschmidt and Peters[669] pointed out that the boron incorporated into tourmaline is effectively removed from the geochemical cycle. There is much evidence to support their assertion. The extreme stability of tourmaline and its resistance to chemical and mechanical weathering processes have been long known and abundantly documented[1344–7, 1350–3, 1358]; many other references exist. Of all the heavy, non-opaque, clastic minerals only zircon has greater stability and resistance.[1287, 1351] Some alteration of tourmaline in the weathering profile of an iron ore deposit (during bauxitization) has been recorded[1348]; conversely, tourmaline is said to be stable under conditions of laterite weathering and preserved in bauxite as a relict mineral.[1355] Some replacement or regeneration of tourmaline may occur in pneumatolysis, greisenization, or progressive metamorphism[1354, 1357]; see below. Replacement (often pseudomorphous) of tourmaline by quartz[1176, 1360, 1361], lepidolite[671, 1177, 1343], muscovite[671, 1351], biotite[1186], chlorite[671, 1348], cookeite[671, 1182, 1356] and albite[1359] have been noted. These examples notwithstanding, much boron is locked within the tourmaline structure for considerable periods of geologic time. As an example, tourmaline from tourmalinized Late Precambrian rocks of southern England and north-west France has been dated to 482±19 million years by the ^{40}Ar/^{39}Ar method.[1342]

Many syntheses of tourmaline show that it forms at temperatures from about 250° to 600°C at fairly low pressures (0·5 to 2 kb) in weakly acid to weakly alkaline solutions.[1263–9] All workers note that tourmaline does not form in strongly alkaline (or acid) solutions, which fact undoubtedly accounts for the absence of authigenic tourmaline in evaporite deposits such as the Green River Formation, the Kramer borate deposit, etc., where other authigenic borosilicates are known. Apparently tourmaline can form at lower temperatures in the sedimentary environment.[1270] Tourmaline replacing anhydrite and occurring as doubly-terminated crystals in halite has been described.[1213]

Tourmaline may be locally abundant in the greenschist facies, making up as much as 90 to 95% of the layers of some schists.[1271] Recent studies have shown that tourmaline in New Zealand schists is about as abundant as glaucophane is in glaucophane schists (Clark Blake, personal comm., 1972). In general the abundance of tourmaline is directly related to the original content of the metamorphosed sediments.[1272, 1321] That much tourmaline results from isochemical metamorphism is demonstrated by its common association with graphite, carbonaceous inclusions, and contents of trace elements such as vanadium and chromium in metamorphosed organic shales.[755, 1270, 1273–5, 1320] Widespread distribution of the mineral throughout a body of schist is another often-cited point of evidence.[1281] The tourmaline formed reflects its pelitic parentage in being of dravite-schorl (that is, magnesium–iron tourmaline) composition with uvite (calcium–magnesium tourmaline) often reported as a minor constituent. Overgrowths of tourmaline on detrital nuclei are very commonly reported[1270, 1272, 1277, 1286, 1288, 1289, 1362] but are statistically rare in occurrence.[1277] The ratio of the overgrowth to the nucleus can be used as a metamorphic indicator, the proportion of the rim increasing with grade of metamorphism.[1206] One report of clinozoisite as an overgrowth or reaction rim on detrital grains of tourmaline appears to be unique.[1204] The association of nearly colourless, possibly manganese-bearing tourmaline (tsilaisite) with piemontite has been mentioned by several authors.[1276, 1278–80]

Tourmaline appears to be stable, with increasing pressure, to the lower part of the eclogite facies (although rare as only one occurrence has been reported[1217]) or, with increasing temperature, into about the middle part of the granulite facies. Only a few studies have been made of the stability of tourmaline at higher temperatures and pressures.[1207, 1216, 1269] Robbins and Yoder[1216] studied natural and synthetic tourmalines (of dravite composition) at various temperatures and at pressures up to 5 kb. At temperatures above 865°C and pressures up to 2 kb the main decomposition products are cordierite, liquid, gas and an unidentified crystalline phase. Above 895°C, at 5 kb, the assemblage kornerupine + sapphirine + liquid + gas is formed. At 925°C and 5 kb kornerupine is no longer stable and the phases coexisting in equilibrium are sapphirine + liquid + gas. The associations tourmaline + cordierite, tourmaline + kornerupine + sapphirine, and cordierite + kornerupine + sapphirine have all been reported.[1168, 1290–1300] A later study by Fuh[1207] generally confirmed these results except that he reported the iron–aluminium spinel, hercynite, to accompany cordierite as a breakdown product. From the X-ray data given in this study it seems possible that sapphirine may have been misidentified as hercynite. Thus tourmaline is successively replaced by kornerupine and sapphirine in the higher granulite facies. Boron contents drop from about 10% of B_2O_3 in tourmaline to a range of about 1–4% in kornerupine (boron-free kornerupine has been synthesized but never found in rocks[1295]) and range from zero to a maximum of 0·75% in sapphirine. While tourmaline and kornerupine are absent in the highest-grade granulites, sapphirine persists and may be present under the temperature and pressure conditions obtaining in the lowermost crust or upper mantle.[1299, 1324, 1363, 1364] This mineral appears to be the last main refuge for boron under these extreme conditions. Unfortunately, there are few available data on the boron content of sapphirine (see Table XXIII). It is also possible that boron may be present in elemental substitution or mineral impurities in the graphite found in granulites and charnockites[593], although Hahn-Weinheimer[534] found no direct relationship between boron and carbon in eclogitic rocks. Dumortierite may also be found in the lower granulite facies in alumina- and silica-rich rocks.[1153, 1203, 1302–7] In at least one occurrence dumortierite was considered to have formed from earlier tourmaline.[1203] Axinite is rarely found in regionally metamorphosed rocks.[332, 1186, 1302, 1367–70, 1373] In any event most accounts agree that boron follows the course of other mobile components and is drastically depleted during progressive regional metamorphism.[444, 495, 617, 755, 835, 1282–5]

(II) ROCK/WATER INTERACTION AND BORON DURING REGIONAL METAMORPHISM

The illite–muscovite transition during diagenesis and early metamorphism is the important mechanism by which boron is released from sediments to the hydrologic cycle or becomes fixed in tourmaline. Althaus and Johannes[1250] using sodium chloride solutions at 1 kb pressure and temperatures from 350° to 550°C to react with illite, glauconite, or montmorillonite, found that the 2M muscovite formed as a reaction product. This is in accord with previous studies on natural pelitic sediments (see above). Studies by several New Zealand workers[478, 703, 1202, 1205, 1211] have shown that hot saline solutions are capable of leaching large proportions of the boron, chlorine, ammonia, lithium and other constituents from a wide variety of rocks present in the New Zealand geothermal field. Significant boron is removed at temperatures as low as 200° to 300°C, the efficacy of the process increasing with rising temperature. Almost all of the surfacially adsorbed boron is removed by this process, but the boron apparently bound within silicate structures, volcanic glass, etc., is not removed until near-melt temperatures are attained. They have shown that this leaching process could account for the composition of the thermal waters found in the New Zealand geothermal field. Waters of similar composition have been described by White[1126, 1219–21] as being possible 'metamorphic waters'. Further studies of such waters ([1201, 1215], and others) indicate that the common characteristics of these waters are high contents of bicarbonate, boron and ammonia ions, nearly neutral pH and temperatures only a little above mean annual temperature. A high boron:chloride weight ratio is also characteristic of such waters and a high boron: potassium ratio may be significant. Meagre data from New Zealand[1210] indicate that the boron:chloride ratios of the springs have been quite constant since records were kept (from about 1937 to present).

(III) BORON IN CONTACT METAMORPHISM

In contrast with regional metamorphism, which occurs over broad areas at relatively high pressures and low temperatures, contact metamorphism is distinguished by local effects (from a few mm to several km) at relatively high temperatures and low pressures, occurring at or near the contact of an intrusive (or extrusive) magmatic body. The effects of metamorphism vary in magnitude and intensity depending upon the depth of emplacement of the magmatic body and the nature of the invaded country rock.[444, 1234, 1313, 1412] Metamorphic changes are produced by the heat and fluids emanating from the magma and are generally allochemical (metasomatic) in nature, although isochemical changes (disregarding water content), due entirely to thermal effects, may occur. Contact metamorphism has been thoroughly reviewed in a monographic study by Reverdatto[1412] which may be consulted for further details.

Boron arrives in contact metamorphic rocks by two main processes which may operate in unison or independently. In the first instance, the element is concentrated in the residual melt of an intrusive magma[838] and is transferred, along with other volatiles such as water, carbon dioxide, hydrogen fluoride, hydrogen chloride, etc., to the invaded country rock; in the second, pre-existing boron in the country rock is mobilized in the metamorphic process. Boron, together with lithium, tin, lead and other metals may be diffused from the country rocks and then assimilated by the intrusive magma. The mobile elements are thus transported from the country rock to the hydrothermal vein systems.[544, 1385] The overall boron content of the intruded rock is generally lowered by contact metamorphism.[444, 617, 835, 1282–5] Boron contents of various facies of contact-metamorphic rocks, studied by Harder[444], range from a high value of 750 p.p.m. of boron (in a weakly metamorphosed pelitic schist) to a low value of 30 p.p.m. (in an argillite contact fels). While boron is found in substitution in silicate minerals of contact-metamorphosed rocks (Table XXIII), most of the boron is present as independent borosilicate and borate minerals. Common borosilicate minerals are, in approximate order of abundance, tourmaline, axinite, datolite, and danburite; less common to rare are grandidierite, serendibite, and harkerite. The most important borate minerals are ludwigite, vonsenite, fluoborite, and szaibelyite (others are listed below and in Table XXIX, p. 112). The borosilicates are found in hydrothermal veins, contact aureoles, and skarns, whereas the borates essentially are restricted to skarns (for example, see [783]).

Skarns are metasomatic rocks consisting of magnesium–calcium–iron silicates and aluminosilicates formed in high-temperature zones of contact halos as the result of interactions between essentially carbonate rocks and magmatic solutions[1409, 1412]; borates are localized with various ore minerals in skarns (see discussion p. 113). As noted by Reverdatto[1412], the literature on skarns alone contains some thousands of names (and most of these are Russian, for skarns represent a commercial source of boron and other elements in the U.S.S.R. and consequently they have received extensive study in that country). In addition to the important review of skarns by V. A. Zharikov[1409], there are general references on skarns and attendant boron mineralization and geochemistry.[891, 1199, 1244, 1249] The following discussion of boron in skarns is necessarily oversimplified.

There are two principal groups of skarns: magnesian and calcareous.[340, 1199, 1409, 1412] Magnesian skarns are formed by the replacement of dolomite or other magnesium-rich rocks at abyssal depths by plutonic intrusive rocks at relatively high temperatures.[340, 1232] Calcareous skarns originate by the alteration of limestone, terrigenous carbonate, or volcanic carbonate rocks at hypabyssal (intermediate) depths ordinarily in the post-magmatic stage at relatively low temperatures.[340, 1199, 1412] The twofold division is important for the commercial deposits of boron, with few exceptions[1230], are found in the magnesian skarns.[343, 1199, 1232, 1409] Boron minerals occurring in magnesian skarns include azoproite, fluoborite, harkerite, hulsite, jimboite, kotoite, kurchatovite, ludwigite, orthopinakiolite, pinakiolite, sakhaite, serendibite, sinhalite, suanite, szaibelyite, tourmaline, vonsenite, warwickite, and wightmanite.

As noted above, the ludwigite–vonsenite series are the commercially most important borate minerals in magnesian skarns. Aleksandrov and others[1199, 1223], expanding an hypothesis originally proposed by Marakushev[326, 1233], show that the parageneses and compositions of minerals associated with the ludwigite–vonsenite series in magnesian skarns can be correlated with the iron content of the ludwigite. Thus, with the iron content expressed as $f = \mathrm{FeO}/(\mathrm{MgO} + \mathrm{FeO})$ (contents in mol.-%) there is a distinct separation between the magnesioludwigite ($f = 0$–25%), ludwigite ($f = 25$–75%), and vonsenite ($f = 75$–100%) parageneses. Associated minerals considered in these parageneses are those typically found in high-temperature magnesian skarns: kotoite, suanite, fluoborite, forsterite (olivine), minerals of the humite group, pyroxenes, garnets, idocrase, amphibole, tourmaline, magnetite, periclase, carbonates, and silicoborocarbonates (sakhaite, harkerite). A relationship between the composition of the borates and the silica content of the medium was ascertained by a diagram of mineral parageneses plotted in coordinates of the log (silica activity) against the log (boric oxide activity). Further experimental data on the influence of f, boric oxide activity, and other physicochemical conditions are given by Nekrasov[1235] and others.[324, 333, 784, 1242, 1409, 1412] Other selected references on magnesian skarns[327, 334, 337, 346, 349, 353, 354, 355, 359, 778, 789, 878, 886, 1224, 1225, 1233, 1238, 1240, 1241, 1246, 1247] may be consulted.

Boron minerals present in calcareous skarns are: axinite, cahnite, calciborite, danburite, datolite, frolovite, korzhinskite, nifontovite, nordenskioldine (occurs especially with borosilicates[1229]), olshanskyite, pentahydroborite, sibirskite, szaibelyite, tourmaline, uralborite, and vimsite. Boron mineralization is superposed (i.e., postmagmatic) upon calcareous skarns, skarn-like rocks, and hornfels. Boron-bearing calcareous skarns are commonly found on limbs of synclines and anticlines especially where the metamorphosed rocks are broken by fractures and faults.[782] In a typical occurrence[780, 1226], boron mineralization took place in three stages: first, the formation of a skarn composed chiefly of wollastonite, manganhedenbergite, and andradite; second, the introduction of the borosilicate minerals axinite, danburite, and datolite; and third, the deposition of calcite, fluorite, and boron-bearing apophyllite (see Table XXIII). The borate minerals commonly occur replacing calcite as pockets, veinlets, and small lenses.[1229]

In some calcareous skarns boron (and beryllium, lithium and fluorine) do not form independent minerals, but are found in substitution in various silicate minerals, most notably idocrase, which contains three to five times more of these elements than associated garnet or pyroxene[781] (and see Table XXIII). The boron content of some skarn minerals can be used as a guide in prospecting for concentrations of boron.[357] The association of tin with boron in both calcareous and magnesian skarns has been discussed by Nekrasov and co-workers[1235–7] and by Shabynin.[787] Further references on calcareous skarns are:[341, 344, 345, 1048, 1222, 1227, 1228, 1231, 1239, 1243, 1410]. For additional general references on both magnesian and calcareous skarns see:[336, 356, 788, 891, 1229, 1244, 1245, 1248, 1249, 1318].

(IV) BORON IN SERPENTINITE

The boron content of ultrabasic rocks has been found to increase upon serpentinization.[490, 513, 542, 790, 1322, 1323, 1326, 1417] The absolute boron content depends upon the character of the primary ultrabasic rock rather than upon the degree of serpentinization; higher values are found in serpentinites formed from peridotites than from dunites.[542] Boron present in serpentinites may be present as boric acid solutions in zeolitic water[513,542], bound within the serpentine structure itself[542,1326], and as independent boron minerals such as szaibelyite[513,1326] and datolite.[1186] As in the case of other metamorphic rocks there is disagreement as to whether boron in serpentinites is supplied by a magmatic source (in this instance by ultrabasic rocks) or arises from enclosing sediments. Some boron may be released through the conversion of ludwigite to szaibelyite.[513] Thompson and Melson[1408] have suggested that serpentinization of oceanic crusts was accomplished by boron-containing juvenile solutions which also furnished boron to the ocean.

Boron in Coal

Coal is the naturally-occurring rock-like black to brown derivative of forest-type vegetation which has been buried, compressed, and altered to a solid material of high carbon content, containing varying amounts of organic compounds. Gold-

Table XXIV.—Boron in Coal

Location	Boron content, p.p.m.		Reference
	In coal	In ash	
U.S.A.			
Northern Great Plains	116		579, 924, 925
Appalachians	25		
Eastern Interior		2200	920, 922
Western	33		
West Virginia		80–960	589, 600
N. and S. Dakota, Texas and Colorado		100–10,000	598
Canada			
Nova Scotia	6–25	52–220	599, 603
British Columbia, Yukon and N.W.T.	'Detected'		601
New Zealand			
North Island	0–465	0–14,900	610, 1064
South Island	0–240	0–4300	
Australia (*NSW*)	2–300		577, 602
Falkland Islands (*metamorphosed*)		20–250	605
South Africa			574
Transvaal	12–68		
Natal	11–89		
Orange Free State	84–109		
India (*Assam, Bengal, Bihar, Hyderabad*)	'Small trace'		609
North Wales (*Vitrain*)		100–1000	616
Germany and England		3100	612
Germany (Ruhr)	3·5–6·0		1009
Germany	5–420	70–10,000+	572
Austria	600 max.	4600 max.	593
Czechoslovakia (*Handlovia*)	51–644		585
Poland	3·8–20·1		575, 576
Coal-tar from above	0·2–3		
Coal-tar coke	0·8–16·6		
E. Germany (*lignite*)	2–236 3–90 mostly		573, 582
Lusatia		99–105	620
Spitzbergen		1000–20,000	595
Portugal (anthracites)		10–1000	583, 604
U.S.S.R.			916
Angara-Chulum Depression			
Coastal-Oceanic	87–146		
Alluvial-Coastal Oceanic	24–53		
Lacustrine	8–36		
Transbaikal	10–100		909
Kubulkei Syncline	78	2270	
Don and Kuznetsk Basins		up to 10,000	606

schmidt and Peters in 1932 discovered the presence of boron in coal ash[612]; since that time a number of coals have been investigated. Many metallic elements have been found in coal and coal ash[923], some of which are extracted commercially[897]; to date the commercial extraction of boron has not proved economical.[589]

The boron content of coal and the associated sediments is related to the paleo-salinity.[577, 902, 909, 1009] The coal-forming vegetation is at least a partial source of boron.[611, 613] The boron content of coal is considerably higher than that of the earth's crustal average, the coefficient of enrichment being about 10^2 to 10^3.[588, 589, 615, 662] The boron content of most coals is in inverse ratio to the ash content[572, 1064], and is largely confined to the organic material present.[575, 578, 587, 597, 909, 910, 916, 923] In many coals the boron is contained almost entirely in the vitrain.[591, 613] 'Boron contours' have been established for some New Zealand coals, where additional boron may have been introduced by hot-spring activity after coal formation; the North Island coals have more than twice the boron content of coals found on South Island.[1064] The boron in most coal is non-volatile[575], although if fluorine is present half or more of the boron will volatilize on burning.[574] In coal ash most of the boron is water soluble if it has not been heated above 800°C.[1064] In some coalfields the boron content, in conjunction with the lead and to a lesser extent the beryllium content, can be used for correlation and identification of non-fossiliferous formations.[290, 905, 1009] In some peat and low coals the boron content increases with depth and degree of decomposition of the peat.[594] The distribution of boron in North American coals follows a lognormal pattern.[1071]

Boron compounds resulting from the combustion of coal will condense (with the ash) on boiler tubes, contributing to the lowering of efficiency of the boilers.[600] The boron content of coal becomes extremely important when coal is used to make graphite for electrodes or atomic reactor components.[573]

The boron content of some coals is given in Table XXIV. Additional information on the subject will be found in references [580, 581, 584, 592, 614, 769, 901, 919, 980].

Boron in Petroleum

Data on the boron content of petroleum are few, although a considerable volume of literature has appeared concerning the boron content of the associated oil-field brines. The available data are mostly concerned with Soviet Russian oilfields.

In many oilfields the boron content of the petroleum decreases with stratigraphic depth, whereas the reverse is true for the associated brines, which tend to become increasingly alkaline with depth[900, 913]; in some areas the older oils are higher in boron content than the more recent oils.[596] The distribution of boron between the oil and aqueous phases is little understood[900], but it is probably an equilibrium factor. Since petroleum is presumed to be of biogenic origin, much, if not all, of the boron content may be primary, although some of it may have been derived from the host rocks.[607, 608, 903] Methanic (paraffinic) petroleums are lowest in boron content, and naphthenic (asphaltic) oils are highest.[904] The boron content of the resinous or waxy fractions is higher than that in other fractions.[903, 904] An example is furnished by an oil from Podkirmakinsk formation of the Lake Artema field, as shown in Table XXV.

Table XXV.—Boron in Petroleum Components[903]

Component	Boron content, p.p.m.	% of sample	% of total boron content
Whole petroleum sample	0·466	100	100
Saponifiable wax	0·316	20·52	67·8
Unsaponifiable wax	0·113		24·2
Asphaltenes	0·008	0·008	1·7
Residual oil	Trace	78·60	Trace
Unaccounted for	0·029		6·3

The boron content of petroleum ash approximates that of the earth's crust.[621] Some of the early values for the boron content of petroleum may be low due to boron loss by volatilization during conventional ashing prior to analysis; the preferred technique employs oxygen-bomb combustion, whereby all of the boron is recovered.[903] Attempts have been made to produce a boron-free petroleum coke which could be graphitized for atomic reactor and spectrograph electrode use, but the coke contains 0·1 to 0·8 p.p.m. boron.[590] Some published values for boron in petroleum are given in Table XXVI.

Table XXVI.—Boron in Petroleum

Location	Boron content, p.p.m.	Reference
Lower Volga	0–0·003	623
Azerbaijan and Volga-Ural region	7–104	903
Kum-Dag and Nebit-Dag, Turkmenia	0·3–3·0	904
Dagestan (petroleum ash)	12–1219	596
Utah (oil shale)	136	619
Alaska (oil shale)	500	898

Additional references on the subject include [233, 899, 911, 912, 915].

Boron in Soil

Soils are formed by rock weathering and alteration by physical, chemical, and biological forces to such an extent that they will support rooted plants. As such, they are of diverse types, and the boron content is at least as varied as that of the parent rocks; the soil boron content is often greater than that of the parent rocks. Soils formed from the weathering of marine sediments and volcanic formations are considerably enriched in boron.[622]

The earth's soils may be divided into two types which are differentiated by their boron content: low boron content (below 10 p.p.m.) and high boron content (up to 100 p.p.m. or more). The low-boron-content soils are most of the soils of the earth, some of which are boron deficient, and are often found on ancient plains, and include most 'wet' areas. The high-boron-content soils include the regions of recent volcanism and boron salinization, such as the Great Basin and Mojave Desert areas of western U.S.A., and a band across the Mediterranean through Turkey, Iran, and the Aral-Caspian lowlands of Kazakhstan.[622, 885]

Normally only soluble boron can be utilized by plants.[662] Since boron occurs in soils in both soluble and insoluble form, this must be taken into account when considering the suitability of a soil for a particular crop. The soluble boron is usually about 10% of the total.[622] The availability of boron for plants depends on several factors, which include the following:

1. *The calcium: boron ratio.* An excess of soluble boron can injure young plants; sufficient calcium can convert the soluble boron to the slowly soluble calcium form, preventing boron injury and supplying boron to the plant for a longer period of time.[586]
2. *The humus content of the soil.* Soils rich in humus lose boron by the formation of easily soluble organic boron compounds, particularly in non-alkaline soils; boron is then lost by leaching or plant absorption.[586]
3. *The percentage of boron 'locked up' as tourmaline.* Some of the boron present in soils is gradually incorporated into authigenic tourmaline, which is very refractory and extremely resistant to weathering. The boron is thus effectively 'locked up' and unavailable for plant use.[662]

In addition to the boron derived from the parent rock, boron is contributed to soils by irrigation and flood water, rain, decomposed vegetation, fertilizers, etc.

Table XXVII.—Boron Content of Soils

Location	Boron content, p.p.m.		Reference
	Acid soluble	Total	
U.S.A.			1078
Podzols	1·0–2·4	10–36	
Grey-brown podzolic soils	5·4–64·8	35–68	
Red and yellow podzolic soils	0·8–63·0	6–63	
Half-bog, Ground-water podzols, and Muck soils	0·8–5·6	14–32	
Prairie, Chernozem, and Brown soils	12·0–39·4	22–41	
Red Desert soils	5·4–13·8	6–15	
Non-calcic Brown soils	3·0–14·4	4–98	
Alluvial soils	6·8–45·5	13–88	
India		0·3–9·9	887
India (Gujarat and Saurashtra)		0·2–1·5	434
India (Bengal)		0·4–2·0	424
India (many kinds of soils)		6·6–66·1	435
India (Limbdi and Vicinity)		454	809

Location	Water soluble	Total	Reference
India (Punjab), Saline-Alkali, 0–6″	1·2–4·8		395
Inner Mongolia		46	367
Iraq		0·1–12	1073
Italy (Apulia)		0·13–1·38	422
(Bari)		0·65 av.	
(Taranto)		0·44 av.	
Italy (Liguria)	0·10		439
Karelian Aut. S.S.R.	<1	<10	413, 419
Latvia	0·02–2·0	1·5–35	389, 392, 420
Lithuania		0·11	406
‘Middle Asia’		112	907
Norway		0·14–0·39	402
Poland	0·04–0·98	2·3–56	373, 374, 383
Romania (Moldovite Basin)		25–32	918
Sardinia		‘small amount’	940
Spain (Salamanca)	0·06–0·78	4·2–18·2	400
U.S.S.R.			
Azerbaidzhan		8–22·4	411
Baikal Region of Siberia		5–20	371
Bashkir Aut. S.S.R. (Forest Steppe)		25–30	368
Bukhara	0·2–5·7	39·6–272	1055
Forest Steppe		0·27–45	405
Georgian S.S.R. (Western)	0·25–0·70		442
Golodnaya Steppe	0·4–5	110–2210	393
Russian Plain along 40th Meridian		1·2–17	426
Sorochin District		0·53–17	431
Tadzhikistan	0·1–2	45–350	401–32
Tatar Aut. S.S.R.		0·2–1·0	404
Ukraine		0·2–64·4	362, 417, 429
Ural Region	0·23–4·4		397
Uzbekistan	0·025–0·035	31·5–74	372, 410
Volgograd Region	0·15–7·3		398
U.S.S.R.			622
Podzolic Humus-illuvial soils	not detected	trace-3	
Podzolic soils	0·19–0·41	1·5–77	
Forest soils	0·33–0·34	1·2–9	
Chernozem soils	0·32–0·87	4–17	
Chestnut soils	0·39–1·1	1–12	
Serozem, Solnetz, Solonchak soils	0·48–18	18–220	
Red soils		1·5–6	

Clayey soils tend to accumulate boron by fixation, whereas sandy soils do not.[392,441] The soil pH usually has little correlation with the boron content[424]; however very acid soils are usually also very low in boron content.[1078] The average total boron content of the soils of the U.S. is about 30 p.p.m.[1078]; that of all soils of the earth is from 10 to 20 p.p.m.[622] Applied boron tends to migrate downward with time, faster and to a greater extent in sandy soils than in clayey soils[383,441]; this is especially notable in wet climates. The sandy soils of West Pakistan, for example, are largely deficient in boron owing to rain leaching and erosion.[447] Boron in alluvial soils is usually higher downstream than upstream, following the course of the river.[383] Where sufficient calcium sulphate (gypsum) is present, water leaching is effective in removing excess boron; this principle has been utilized in the Coachella Valley of California.[418]

A listing of some of the published values for the boron content of soils is given in Table XXVII.

Whetstone et al.[1078] and Vinogradov[622] show the boron content of many soils from diverse locations and have extensive bibliographies. Other references concerning boron in soil include the following: [360,361,363–6,369,370,377–82,384–8,390,391,394–6,399,403,407–9,412,414–16,421,423,425,427,428,430,433,436–8,440,443,445,446,791–8,800–6,808,810–12,1002,1005,1059,1062,1076].

BORON ISOTOPE RATIOS

Boron occurs naturally as a mixture of two stable isotopes, boron-10 and boron-11, contained in many minerals wherein boron is an essential constituent, and also in many other minerals (and rocks) in trace amounts, with the boron substituting for silicon or aluminium (see Boron in Sedimentary Rocks, above). The cosmic ratio of $^{11}\text{B}/^{10}\text{B}$ was calculated to be 4·33 by Suess and Urey in 1956[672] from theoretical considerations. In 1946 Ingram obtained the value of 4·311 for this ratio, using commercially available boron trifluoride in a mass spectrograph[1065], measuring mass numbers 48 and 49 for BF_2^+. Since then many researchers have re-determined this ratio, using improved instruments and techniques. It has been found that boron trifluoride is not an ideal substance for use in a mass spectrograph, as it has a 'memory effect', and attacks glass, quartz, and diffusion-pump oil, causing the introduction of impurities which affect the values obtained.[927,933,1067] Boron trichloride is found to be superior to boron trifluoride in the respect that it is less reactive towards components, but it causes difficulty due to the high incidence of interfering ions.[927] Other 'gaseous' preparations were utilized, such as methyl borate[1058,928], boron hydrides[1058], etc., but the greatest advance came in about 1960 with the development of a 'solid source' mass spectrograph. Since then a number of workers have studied this problem, using borate and boron-bearing minerals and rocks from world-wide sources, as well as meteorites, utilizing the technique pioneered by McMullen et al. in 1961, measuring Na_2BO_2^+ ionic peaks at mass numbers 88 and 89[141], and using sample preparation techniques which avoid isotope fractionation.[1066]

Several authors report no variation of the $^{11}\text{B}/^{10}\text{B}$ ratio using different minerals as a boron source[927,928,1067], whereas others, using what might be considered more reliable preparation methods and the 'solid source' technique, find real differences in this ratio for different minerals, even when from the same source.[932,1057,1066,930] Variation in the $^{11}\text{B}/^{10}\text{B}$ ratio has been noted in the same mineral from different horizons but the same location.[141,926] Differing instruments and instrumental operating conditions also produce significant differences in this ratio, as great as 0·112.[1057]

Boron is a highly mobile element, and as such it has been suspected that isotope fractionation could occur as a natural geochemical process, during and since degasification of the mantle.[926,929,934] Siberian kimberlites and meimechites have been shown to be enriched in boron-11 as compared to basalts, and suggest a $^{11}\text{B}/^{10}\text{B}$ vertical gradient within the mantle.[926] Recent laboratory experiments have

Table XXVIII.—Boron Isotope Ratios

Rocks and sea water

Method*	Material	Place of origin	$^{11}B/^{10}B$	Reference
(c)	Kimberlite	Siberia	4·115	926
	Meimechite	Siberia	4·118	
	Picritic Basalt	Siberia	4·060	
	Polphyric Basalt	Siberia	3·972	
(a)	Gabbro	Insizwa (Japan)	4·102–4·108	930
(a)	Basalt	Hawaii	4·051	931, 1068
	Basalt	Mohole Project	4·042	
	Gabbro	not given	4·092–4·104	
	Slate (Paleozoic)	not given	4·100–4·108	
	Granite G-1	U.S.G.S. Standard	4·063–4·066	
	Diabase W-1	U.S.G.S. Standard	4·039–4·054	
	Sea water	Pacific Ocean	4·071	
	Sea water	Tokyo Bay	4·020	
(a)	Sea water	Tokyo Bay	4·041	930
(a)	Sea water	Pacific Ocean	4·216–4·223	763
	Sea water	Atlantic Ocean	4·214	
	Sea water	Arctic Ocean	4·236	
	'Terrestrial rocks' mean		4·029	

Minerals

Method	Mineral	Source	$^{11}B/^{10}B$	Reference
(a)	Colemanite	California, Turkey	3·995	1066
(a)	Colemanite	Turkey, Argentina, California	3·991–3·993	930
(a)	Tincal (Native Borax)	Searles Lake, Calif.	4·068–4·072	141
(a)	Borax from brine	Searles Lake, Calif.	4·040	141
(b)	Borax from brine	Searles Lake, Calif.	4·370	1057
(b)	Tincal	Tibet	4·326	1057
(a)	Tincal	Argentina, Kashmir	3·981–4·033	930
(a)	Tincal	California	4·24	1068
(a)	Inyoite	Turkey	4·037	930
(a)	Inyoite	Kazakhstan	4·141	1066
(a)	Ulexite	Argentina	3·922	1066
(b)	Ulexite	Argentina	4·270	1057
(a)	Ulexite	Argentina, Turkey	4·069–4·073	930
(a)	Datolite	New Caledonia	4·057–4·061	930
(b)	Sassolite	Tuscany	4·411–4·416	1057
(a)	Sassolite	Japan, Italy	4·073–4·121	930
(a)	Pandermite (Priceite)	Turkey	4·069	930
(b)	Pandermite (Priceite)	Turkey	4·291–4·297	1057
(a)	Hambergite	Madagascar	4·026	1066
(a)	Szaibelyite	B.C., Canada	4·064	1066
(a)	Howlite	California	3·962	1066
(b)	Kernite (Rasorite)	California	4·322	1057
(b)	Boracite (Stassfurtite)	Germany	4·422	1057
(a)	Hydroboracite	Argentina	4·061	930
(a)	Tourmaline	Finland	4·005	930
(a)	Kotoite	Korea	4·045	930
(a)	Inderite (Kurnakovite)	Argentina	4·069	930

* Procedures used: (a) $Na_2BO_2^+$, mass 88 and 89. (b) BF_2^+, mass 48 and 49. (c) Method not stated.

Table XXVIII.—(continued)

Meteorites			
Method	Name and type	$^{11}B/^{10}B$	Reference
(a)	Toluca Iron	3·85	1068
	Richardton Chondrite	3·81	
	Ehole Chondrite	3·82	
	Achilles Chondrite	3·90	
	Pasamonte Achondrite	3·96	

confirmed that it is possible to effect an isotope enrichment using a borate solution and a clay column[1077]; sea-water is about 2% enriched in ^{11}B, owing to selective adsorption of ^{10}B by illite in the oceans.[763]

The $^{11}B/^{10}B$ ratio as determined by various workers is shown in Table XXVIII. Method (a), measuring the $NaBO_2^+$ ionic peaks at mass numbers 88 and 89, gives what are generally agreed to be the most reliable values. Considering only the values for the $^{11}B/^{10}B$ ratio as determined by this method, it is apparent that there is a real difference in different minerals, and perhaps a constancy for any given mineral wherever found.

CONCENTRATION OF BORON

Boron has been locally concentrated by a number of geochemical processes, resulting in several distinct types of deposits. These include the following:

I. *Endogenetic Processes*
II. *Metasomatic Processes*
III. *Exogenetic Processes*
    A. Mechanical Concentration
    B. Chemical Precipitation
        1. Halogenetic Concentration
            (a) Marine Evaporites
        2. Volcanogenetic Concentration
            (a) Soffioni
            (b) Borax Lakes
            (c) Playa Deposits
            (d) Bedded Lacustrine Deposits
                (1) Calcium Type
                (2) Sodium Type
                (3) Magnesium–Calcium Type

All major and many minor boron concentrations occur along extensive deep-seated fault systems, where the Cenozoic tectonic-volcanic belts pass through regions of arid climate. These have been described as the Pacific Ocean Boron Belts, producing the Cordilleran Borate Province with its exogenetic manifestations in North and South America and endogenetic deposits in Asia, and the Mid-Asiatic or Mediterranean Boron Belts with their Mediterranean Borate Provinces. (See map, Fig. 3.) [823, 885, 891, 1035, 1051, 1106]

I. Endogenetic Processes

Endogenetic processes include crystallization from melts, such as in igneous rocks and pegmatites, as well as precipitation from solution, generally at elevated temperatures. Most such occurrences are where sediments are intruded by granitic rocks.[878] When magmas crystallize, much of the retained boron is concentrated in the residual melt, and upon final solidification forms borosilicates such as tourmaline, particularly in the upper portions.[823, 1035] At depth borates of iron, magnesium, and manganese are formed.[883, 886, 891] Concurrently or subsequently high-temperature minerals may form in metalliferous veins of the pneumatolytic-hydro-

Refs. p. 120

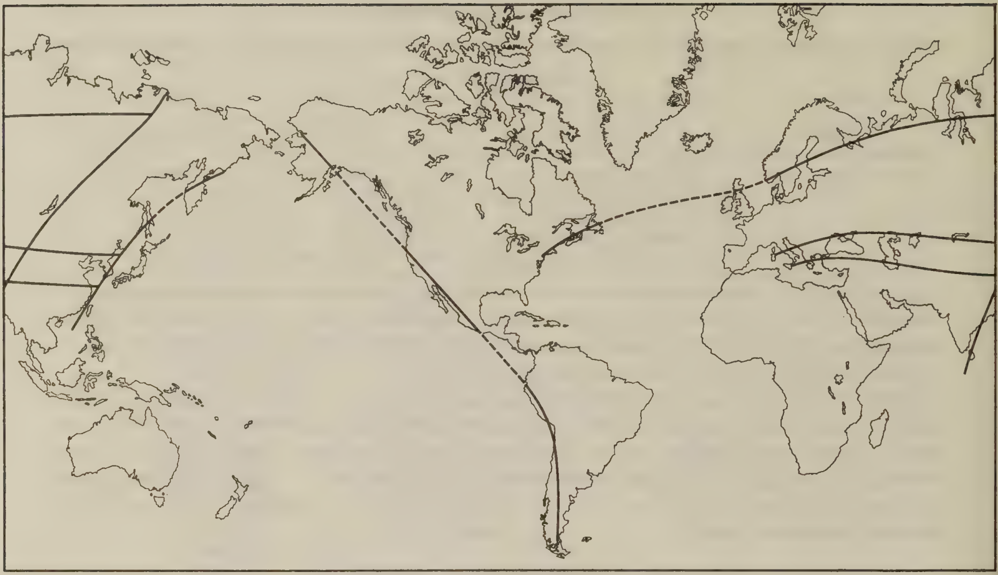

FIG. 3.—Boron belts of the earth

thermal type.[1035] Hypogenetic reactions occur within the earth under reducing conditions, and derivatives of gas-water-acidic reactions have given rise to many large magnetite-ludwigite ore deposits, as well as forming kotoite, tourmaline, danburite, axinite, fluoborite, etc.[885, 886, 1035, 1095, 1096] Commercial boron production from endogenetic deposits has been minimal, although some progress has been reported in Japan utilizing ludwigite ores[873], and in Russia utilizing datolite ore.[654, 871, 875, 876]

Other references on the subject include[324, 325, 337, 345, 790, 891, 1050, 1194].

Table XXIX.—Some Endogenetic Boron Minerals (Non-Pegmatite)

Mineral	Reference
Axinite	1199
Danburite	1199
Datolite	1199
Fluoborite	886, 1094, 1199
Harkerite	1199
Hulsite	1094, 1199
Jimboite	1094, 1199
Korzhinskite	1094, 1199
Kotoite	1094, 1097, 1199
Ludwigite	886, 1094, 1095, 1096, 1199
Nifontovite	1094, 1199
Orthopinakiolite	1094, 1199
Sakhaite	1199
Serendibite	1093, 1199
Sibirskite	1094, 1199
Sinhalite	1094, 1199
Stillwellite	227, 1199
Suanite	886, 1094, 1199
Sussexite	1094, 1199
Szaibelyite	886, 1094, 1097, 1098, 1099, 1199
Uralborite	1094, 1199
Vonsenite	1094, 1096, 1199
Warwickite	886, 1094, 1199

II. Metasomatic Processes

Metasomatic processes involving the migration of boron-bearing fluids at probable temperatures of 300–500°C are responsible for the formation of magnesium borates from previously formed silicates and oxides in dolomite–granite or magnesite–granite contact aureoles. A similar process has occurred in manganese carbonate ores, particularly in Japan, forming manganese borates. At Hol-Kol in North Korea, and at Yakutia, the boron concentration in dolomite is high enough for commercial boron recovery.[324,1035,1097]

In non-carbonate rocks, borosilicates are formed. Recently, much study has been given to the association of boron with non-borate ore deposits, principally metallics; the boron may have served a fundamental complexing function in the metal migration and resulting formation of many ore deposits.[838,1114] Among these may be mentioned deposits of iron[328,626,633,649,771,946,954,959,964,966,1130], copper[347,348,540,958], gold[935,942], tin[550,657,949,960,967,985], tungsten[329,943,985], lead[864,939], zinc[864,938], barium[937], uranium[948], aluminium[944], rare earths[952,953], mercury[289,773], diamonds[512,1061], manganese[1129], beryllium[952]; also clays[270,742,945], nitrates[957], salines[963] and miscellaneous ores.[325,658,947,955,956,962,986] Boron has been found to concentrate in dispersion haloes around metal deposits, and can be used as an indicator in prospecting.[635,644,649,935]

III. Exogenetic Processes

Exogenetic processes of several types are responsible for most of the industrial or commercially valuable boron deposits currently being utilized. These have been characterized as mechanical concentration and chemical precipitation.

A. Mechanical Concentration

Mechanical concentration processes are best illustrated by the tourmaline sand type of deposit, wherein those rock constituents less resistant to weathering are altered and washed away, leaving behind the highly resistant tourmaline residues. Little use has been made of this type of deposit, although some experimental work has been done in Japan[870,872] and Russia[869,999] on the utilization of tourmaline and datolite concentrates in the production of special glasses and boric acid.

B. Chemical Precipitation

1. Halogenetic Concentration. Magnesium borates predominate.

(a) BORON IN MARINE EVAPORITES

At a number of places in the world there occurs a special type of marine sediment, the sometimes immense buried salt deposits which are the result of sea water evaporation. These are principally of Permian age[144,145,148,164,184,185,194,198,199,224,225], but some are older[685,688] and some younger.[200,687] The most extensively studied are the very large Stassfurt beds of Germany, which are at places over 1000 metres thick and of wide geographic extent[671]; the Yorkshire beds of England may be a part of this same sequence.[225,226] Other somewhat lesser but similar deposits occur in Oklahoma, Texas and New Mexico, also Michigan in the United States; Nova Scotia; the Inder uplift north of the Caspian Sea; Donets Basin; Siberia, etc. The introduction of sea water into the evaporation lagoons may have been continuous or intermittent.[671] The concentration of the dissolved salts increased during evaporation until equilibrium solubility was reached, when precipitation began. A quite regular sequence of beds was formed, giving a series of mineral zones beginning at the bottom with limestone and dolomite, followed by gypsum, anhydrite, polyhalite, potash-free magnesium sulphate, kainite, sylvite, carnallite, and bischofite zones. In some instances evaporation was incomplete.[660]

The phase-rule chemistry of evaporating sea water is quite complex and has been investigated by several authors.[117,143,185,689,1035] A number of minerals are found in each zone, with halite common to all zones subsequent to the lower gypsum zone, which in most places has been converted to anhydrite. Some boron is found with the limestone and anhydrite, partially as adsorbed material in the included clay[936, 200], but possibly also included in the crystal lattice by borate ion replacement of the carbonate ion of the limestone or of the sulphate ion in the anhydrite. Subsequent recrystallization produced boracite from lattice-included boron and danburite from clay-included boron, both of which may be found at some places throughout the sulphate zones.[201, 203] Hydroboracite has been identified at or near the calcium carbonate–sulphate interface near the lower limit of the polyhalite zone.[199, 671] Boron is also found in the potassium-rich zones, but most of the boron, along with the magnesium, remained in solution in the eutonic brine until the bischofite stage was reached, when the magnesium borates formed.[201, 1072]

The formation of the boron minerals in evaporating sea water is evidently a

Table XXX.—Borate Minerals in Marine Evaporites

Mineral	Reference
Aksaite	1136, 1147
Aldzhanite	1147
Boracite	144, 153, 189, 198, 205, 207, 208, 209, 210, 211, 212, 213, 220, 225, 226, 671, 691, 894, 1072, 1147, 162
Braitschite	1079
Chambersite	1137, 1138
Chelkarite	1147
Colemanite*	167
Danburite	203, 215, 223, 688
Ericaite	207
Fabianite	1139
Fluoborite	691
Ginorite	1072
Halurgite	1140, 1147
Heidornite	206
Hilgardite	215, 217, 1072
Howlite	223
Hydroboracite	144, 164, 167, 194, 199, 671, 1072
Inderborite	170
Inderite	181, 190
Inyoite*	154, 167, 222
Ivanovite	1141
Kaliborite (Heintzite)	150, 154, 173, 174, 671, 691, 1072
Kurgantaite	157, 1142, 1148
Kurnakovite	166, 190
Lüneburgite	146, 209, 221
Metaborite	1147
Para-hilgardite	216
p-Veatchite	188, 193
Pinnoite	198, 671
Preobrazhenskite	160, 190, 691, 1072
Priceite*	167, 218
Probertite*	218, 219
Satimolite	1143, 1147
Searlesite	163
Strontioborite	1144, 1147
Strontioginorite	187
Strontiohilgardite	688
Sulfoborite	164, 165, 671, 1072
Szaibelyite (ascharite)	144, 147, 150, 154, 156, 167, 204, 211, 671
Tyretskite	1145, 1148
Ulexite*	144, 167, 194, 218, 223
Veatchite	224
Volkovskite	1146

* These minerals seem to be formed as a result of metamorphism, often with the introduction of extraneous calcium and strontium[202]; at places pseudomorphs of calcite after borates are found.[144]

slow process; experiments produced only a 'gel' which upon dehydration produced anhydrous boracite.[686]

At some locations, such as Nova Scotia and Inder, surface water has caused the hydration of anhydrite to form gypsum. Since boron apparently cannot enter into the gypsum lattice, borates are formed by the boron liberated during the hydration process.[167, 218, 223] At Inder particularly, this process accounts for the formation of commercial concentrations of boron minerals under the gypsum 'hat'.[159, 167, 178] Additionally, already formed boron minerals may undergo alteration as the result of fresh water influence, such as the conversion of kaliborite to szaibelyite[154, 157], and the formation of ulexite, colemanite and other calcium borates from previously existing magnesium borates.[144, 202] Most authorities agree that there was sufficient boron present in the original sea water which evaporated to form the salt beds to account for all of the boron found in these deposits, but some authors disagree, insisting that no boron minerals were formed in saliferous basins without delivery of boron from a separate volcanic primary source.[685]

At the present time it is possible to observe a salt deposit quite similar to those of Permian age being formed in the Kara-Bogaz Gulf where waters of the Caspian Sea drain continually into the Gulf and there evaporate completely. The process is continuous, but seasonally variable. The waters of the Gulf are not uniform in composition, being diluted on the south-west by the influx of Caspian Sea water and subject to intensive evaporation all over the basin, but especially on the east. All stages of precipitation seem to be present simultaneously, from the beginning of halite deposition on the west to the bischofite stage in a side-bay of the Gulf on the north-west side.[200] While the salinity of the Caspian Sea water is only about one-third that of the open ocean, and the element ratio is different[684], the principle is the same.

More than 20 boron minerals which may be considered to be 'primary' are found in salt-bed deposits, plus several which seem to be the result of alteration due to groundwater influences. A listing of published marine evaporite boron minerals is given in Table XXX.

Other references on boron in marine evaporites include the following: [149, 151, 152, 155, 158, 161, 163, 168, 169, 171, 172, 175–7, 179–82, 186, 191, 192, 195–7, 202, 214, 690, 746, 761, 867, 868, 941, 947, 951, 965, 984, 1060, 1127, 1200].

2. Volcanogenic Concentration. Sodium and calcium borates predominate. Several reviews have been published.[561, 671, 839, 893, 884]

(a) BORON IN SOFFIONI, GEYSERS, AND MUD VOLCANOES

These exogenic systems have been described separately above, under the heading of Mineral and Spring Water. Extensive installations in the Larderello area of Italy utilize natural steam for the production of electric power, and boric acid is recovered from the condensate.[453, 463, 989] Since most soffioni, geysers, and mud volcanoes are so situated as to allow essentially complete run-off, few large concentrations of borates from this type of source have accumulated. Exceptions are the deposit of sassolite in the crater of Vulcano on Lipari Island[885], and of borax at the Kertch peninsula.[456, 459] Both of these have yielded commercial quantities of boron minerals.

(b) BORON IN BORAX LAKES

A listing of published data on boron in saline lakes has been given above. However, a few of these merit special attention.

(1) *Borax Lakes of Kashmir and Tibet*

In western Tibet and the adjacent areas of Kashmir and Jammu there are several borax deposits which have been worked since ancient times. These are essentially borax marshes or intermittent lakes fed by springs, where borax (tincal) has formed in layers from stagnant water; in places and at times these layers are up to three feet thick.[671, 885] These deposits are at a great altitude, difficult of access, and have been little studied. Ulexite seems to be absent from these deposits.[671]

(2) *Borax Lakes of California and Oregon*

Borax was discovered in the waters and muds of Clear Lake in 1856, and nearby Alkali Lake (Borax Lake, Lake Kaysa) in 1857, by Dr. John Veatch, who was exploring the area specifically seeking borax. The lake was fed by several nearby borax springs. Commercial borax production got under way in about 1864, and continued for several years until the works were flooded out by the low-borate water of a flowing drilled well.[1100] The only borate minerals found here were borax and teepleite.[110]

Searles Lake, now essentially a playa, is the remnant of a much larger body of water resulting from glacier melting and transport of boron from springs near the north end of Owens Valley. Now dry except following scant seasonal rains, it consists of two porous salt beds separated by a layer of impervious clay. The upper bed is about 75 ft (23 m) thick; the lower bed is about 35 ft (11 m) thick.[142] The exposed bed covers about 12 square miles (31 km^2), but the total area underlain by the brines is about 40 square miles (104 km^2).[1102] Brine permeates the pores, estimated to be about 25% to 40% by volume. Borax crystals are found in the salt mass, along with about 25 other minerals.[109, 128, 142, 1100, 1101, 1115] In addition to borax, three other borates occur here: searlesite, teepleite, tincalconite.[1091, 1115] Large-scale borax production has been carried on here for many years, utilizing only the brine; potash, soda products, bromine, and lithium are also recovered.[650–2] The phase-rule chemistry is very complex.[1110]

Owens Lake, now seasonally dry, was once the terminal basin for the Owens River, which contained a considerable amount of boron (see Boron in Rivers above). With the diversion of water from the Owens River to the aqueduct of the City of Los Angeles, Owens Lake virtually dried up, resulting in the concentration of boron in the residual brine.[128, 1101] Borax was recovered for several years as a by-product of soda recovery.[1030]

At one time borax was recovered from a marsh at the southern end of Lake Alvord, in Oregon.[671]

(3) *Lakes of Mexico*

Lake Texcoco, which in historic times was a fresh-water lake but now is nearly dry, furnishes brines from which in 1942 about 2600 tons of borax could be recovered annually, along with a considerable amount of soda and salt.[997]

(4) *Lakes in the Soviet Union*

A number of lakes in the Soviet Union, particularly in the Ural-Emba interfluve[120–2] and in Central Asia[136] contain sufficient borax in solution to allow borax recovery, but no published record of any production has been noted.

(c) BORON IN SPRING AND PLAYA DEPOSITS

Playa deposits form in basins of internal drainage in areas of arid climate, sometimes with associated alkaline borate springs. Some of these springs are situated close to streams so do not drain into an adjacent playa, but form borate cones and aprons in the immediate vicinity of the springs. Playa deposits are known from Nevada and California (borate marshes), and the Andean Altiplano of Peru, Bolivia, Chile, and Argentina (salares).

The playa deposits of Nevada (Teel's Marsh, Rhodes' Marsh, Columbus Marsh, Fish Lake Valley) and California (Death Valley Floor) were utilized for borate production as early as 1870, and for the following 20 years or so. These borate marshes contain borax crystals and soft nodules of matted silky ulexite fibres, called 'cottonballs', which form in the mud. The ulexite and borax crystallize out around the edges of the marshes from the waters which seasonally flood the playas, and also in the vicinity of springs near the edges of the marshes. There has been no commercial production from U.S. playa deposits for many years.

In South America, on the Altiplano along both sides of the Andean crest, is the Andean portion of the Cordilleran borate province, comprising about sixty known borate occurrences, extending more than 700 miles in a north-south direction.[1086] Most of these deposits are of the playa type, several are of the spring type, and a very few are buried older (bedded) deposits.

The Andean playa deposits, locally called salares, are found in the Peruvian province of Arequipa[112,885,892,1197], the Bolivian provinces of Ouro and Potosí[671,885,1197], the Chilean provinces of Tarpaca, Antofogasta, and Atacama[113,885,890,892], and in Argentina in the area formerly designated as the Argentine National Territory of Los Andes, now included in the provinces of Jujuy, Salta, and Catamarca (the 'Puna').[111,573,655,656,879,883,885,1086] For the most part all of the above are at elevations of from 10,000 to over 14,000 feet (3000 to 4300 metres) above sea level, in a cold, very arid climate. Typically a salar will contain a central salt bed, with ulexite forming in the mud around the edges, from a solution saturated with respect to sodium chloride and sodium sulphate. Gypsum is often an accompanying mineral, but is more prevalent in the Chilean areas, possibly owing to the higher sulphur content there.[1197] Often a salar borate deposit will contain two distinct borate horizons, separated by a layer of sand, overlain by a saline caliche crust, and underlain by travertine, sand, and clays. The upper borate layer, up to about 0·5 metre in thickness, contains 'papas' ('potatoes') or soft ulexite balls from small granule to head size, in a sandy clay. The lower layer, usually somewhat thicker, contains larger lenses and layers of ulexite of a more compact nature.[1086] In addition to ulexite, the only other primary borate minerals reliably reported from the salares are borax[111,656,1086,1088,1092], inyoite[112,113,1086,1089], and possibly kurnakovite.[111,570] Volcanic rocks of Miocene or early Pliocene age underlie many of these deposits, and more recent volcanics are in the immediate vicinity.[112,885,895] At one time or another the ulexite was harvested from many of these salares for borate recovery, but the development of richer and more accessible deposits elsewhere has resulted in the nearly total elimination of borate production from playa deposits. In 1972 borax (tincal) was being harvested from Salar de Pocitos at Carolina in Salta, and cottonball ulexite from Salar de Cauchari at Por Venir in Jujuy.[828]

Similar deposits are known in the Sirjan Steppe in Iran, near Shahrebabak[562,885], but no production is noted.

Spring deposits, particularly in Argentina, consist of cones and aprons of virtually pure ulexite formed around vents, from some of which cool to hot waters are still issuing and still depositing borate. Gas, presumably carbon dioxide, accompanies the water in several locations. The residual solutions, or 'mother liquors' do not accumulate locally, but are carried off by nearby streams, either to lakes or to the ocean. At one place borax accompanies the ulexite. A few spring deposits are being or have been mined; they range in size from a few hundred tons to over 10,000 tons of borate. These deposits have all the diversity of form found among recent calcareous tufa and siliceous sinter deposits; accompanying minerals are a small amount of halite and some calcite, principally as an incrustation.[1197]

(d) BORON IN BEDDED LACUSTRINE DEPOSITS

As used herein, bedded lacustrine deposits include those borate deposits which are obviously of non-marine lakebed origin, as well as some others (which generally show a bedded structure) whose origin is less certain; they may represent ancient playas or spring deposits which have been buried and subjected to tectonic forces. Such deposits are known in several parts of the world. Several types are known, which include the calcium type (ulexite–colemanite), the sodium type (borax–kernite), and perhaps a magnesium–calcium (hydroboracite) type.

(1) *Calcium Type* (*Ulexite–Colemanite*) (Fig. 2, Section A1)

Presumably the borate in the ulexite–colemanite type originally consisted only of ulexite in most deposits, but inyoite may have been a primary mineral in some.[111,112,1089] Subsequent leaching by groundwater and recrystallization converted all or a part of the ulexite to colemanite.[555] In some areas pseudomorphs of colemanite after inyoite have been found.[552] Typically such a deposit will consist of lenticular strata of ulexite and/or colemanite alternating with tuffs, clay-shale, and limestone. Individual borate layers may be as thick as 30 feet (9 m), in lenses up to 150 feet (46 m) thick and $\frac{1}{3}$ mile (540 m) long.[1106] Often the strata containing the borate deposits have been tilted, folded, faulted, uplifted, and somewhat eroded.[1103] Gypsum[671] is associated with many of these deposits; inyoite and meyerhofferite are found in a few.[1082, 1086, 1089, 1104] These deposits are closely associated with volcanic rocks.[553, 554] From the time of their discovery in California in the 1880's until the dawn of the sodium–borate era in about 1926, the bulk of the world's borate supply came from these deposits; some are still being worked. Deposits of this type have been found in California near Death Valley Junction, the Furnace-Creek borate district, and others in the Death Valley area[1102, 1109]; in the Calico Mountains and near Dagget, both close to the present town of Barstow[1087]; at Tick Canyon near Lang[1100]; and in Ventura County in the Lockwood Valley.[1105] In Nevada similar deposits have been described in the Muddy Mountains and Callville Wash, both in Clark County in the vicinity of Las Vegas.[1103] All of these have yielded commercial production at one time or another; only a few are active today.

In South America similar borate deposits of the calcium type are known at Tincalayu and north of Sijes, and also at the Monte Azul mine south of Sijes, all in Salta[1089], and at the Salar de Cauchari in Jujuy.[112] There is no published record of any commercial production from these deposits.

In north-western Turkey, in Anatolia south of the Sea of Marmara, borates have been produced for many years from bedded lacustrine deposits of the calcium type. At Sultanchayir, pandermite (priceite) was mined since the 1860's until the deposit was exhausted.[1080] This deposit consisted of nodules up to a ton in size, found below a layer of gypsum[560, 1083] of Miocene age.[559]

In recent years, several other bedded lacustrine borate deposits of the calcium type have been found in Turkey in a roughly kite-shaped area outlined approximately by lines drawn between Bursa, Balikesir, Isparta, and Eskishehir.[888, 1116] The mineral paragenesis of these deposits parallels that of similar California deposits.[556, 557] The deposit formerly mined at Sultanchayir is within these boundaries, along the Bursa-Balikesir boundary, south of Susurluk.

In the vicinity of Bursa, near the village of Kestelek, there is a deposit consisting of a massive vuggy bed of colemanite 18 to 24 feet (6 to 8 m) thick, with probable ore at 1×10^6 tons; production in 1955 was more than 18,000 tons.[1084]

North of Bigadich about 7 miles (11 km) is the town of Islelkoy, which is at the approximate centre of the borate concession (government lease) consisting of 24 miles^2 (61 km^2), and containing not less than eight colemanite deposits. In three of the mines, beds of ulexite up to 2 m thick have been exposed, with overlying colemanite beds up to 1·5 m thick; the two ores are mined separately. Probable reserves are 3×10^6 tons, with 50×10^6 tons possible.[1083, 1084] At Begendikler (in this concession) the colemanite is found as lenses in flat-lying clay strata[1080], while at Iskelekoy, about $2\frac{1}{2}$ miles (4 km) S.W., and at Faras, about 2 miles (3·2 km) S.E., the strata are folded and faulted.[563, 1084]

At Etibank, about 9·5 miles (15 km) south-west of Emet, about 60 miles (97 km) due east of Bigadich, a large, high-grade colemanite deposit, consisting of nodules and aggregates in beds up to 61 ft (20 m) thick, was recently found by the M.T.A. (Mineral Research and Exploration Institute of Turkey) while evaluating a lignite deposit; reserves are estimated at 5 to 7×10^6 tons. The ore was being mined in an open-cut in 1969[1081, 1082, 1084], but no production figures are available.

Near the city of Isparta a colemanite deposit has been found[1084] but records of reserves and production are lacking.

(2) *Sodium Type* (*Borax–Kernite*) (Fig. 1, Section A1)

Bedded lacustrine deposits of the sodium borate type have been found in California[566, 1107], Argentina[558] and Turkey.[1085] Prior to the discovery of the California deposit in 1925, this type of deposit was unknown. There are no surface indications of the buried deposit; limited mining of peripheral calcium borates (colemanite and ulexite) was carried out during the period 1924–1927.[1198] With the discovery of the extensive high-grade Kramer sodium borate deposit (near the present town of Boron) the production of borax from the calcium borate type of deposit essentially ended in the United States.[566, 874] Substantial reserves remain in some of the calcium borate deposits, but they are lower grade and cannot compete pricewise.[566, 1103]

The Kramer sodium borate deposit is essentially a non-marine shallow water lakebed deposit, roughly oval in shape, about 2 miles (3·2 km) east–west by 1 mile (1·6 km) north–south; it is surrounded by a thin envelope of ulexite and colemanite of about double the above dimensions. The sodium borate ore body is roughly lenticular in form and consists of alternating layers of borax, clays and altered tuffs up to 220 feet (61 m) thick. It is completely buried under 120 to 1000 feet (37 to 300 m) of arkosic sands and clay-shales.[564, 568, 571, 1053] Basaltic lavas underlie at least a portion of the borax deposit.[564, 566, 1053] Early investigators assigned a probable Pliocene age to the deposit using areal correlation; the finding of Middle Miocene mammalian fossils overlying the uppermost borax horizon established the age as not younger than Middle Miocene.[1111]

It is presumed that the borax was deposited directly in a shallow lake from nearby borate springs[566, 567, 1090]; a fresh-water stream may have also been involved.[880, 1090] A remarkable aspect of this deposit is the almost total absence of the assemblage of saline minerals such as halite, trona, gypsum, thenardite, etc., usually found in basins of internal drainage.[567, 1069, 1102, 1108] While much of the borax is in flat-lying beds, there has been some faulting and folding. Locally, some of the borax has been altered to kernite by dehydration and recrystallization with resultant disruption of the original beds.[565, 566, 1053, 1107] Locally kernite has rehydrated to form borax.[569] Individual kernite crystals measuring 8 feet × 3 feet (2·6 × 1 m) have been found. Numerous secondary borate minerals formed along some of these faults.[1112, 1113] Reserves in 1966 were given as 100×10^6 tons[1102], probably a conservative figure. In 1960 this deposit alone supplied an estimated 60% of the world borate requirements outside the Soviet bloc.[1106]

In north-western Argentina, borax is concordantly intercalated with members of the Sijes formation (of probable late Cenozoic age), composed of clastic continental sediments deposited in a closed basin. Lens-like bodies of borax are localized by structural control along the north–south axes of the anticlines, and probably represent old marsh accumulations which were buried, metamorphosed, and deformed by folding and faulting. The principal known lens is at Tincalayu, on a peninsula extending south-westward into the Salar del Hombre Muerto (a large salt pan), at an elevation of some 12,000 feet (4000 m). This is essentially a monomineralic deposit of borax, partly transformed in the lower levels to kernite, with smaller amounts of rarer borates. The borate lens rests on a thick bed of halite, and is overlain by about 50 m of brownish claystones, siltstones, tuffs, and sandstones. The Tincalayu deposit is being actively mined.[558, 1413]

Recently an immense buried sodium borate deposit of the borax–kernite type has been discovered in Turkey near Kirka. This deposit is very similar to the Kramer deposit in California in structure and suite of minerals, but is estimated to contain 400 to 500×10^6 tons; it is therefore about three times the size of the Kramer deposit and is by far the largest borate deposit known.[1085] At the time of writing, development work was just beginning and information on the deposit is scanty.

(3) *Calcium–Magnesium Type* (*Hydroboracite*)

A large bedded deposit consisting almost entirely of hydroboracite, inyoite, and colemanite, has been found near Sijes in the province of Salta in Argentina.[828, 1089] This deposit, while extensive, has not been developed commercially, and little information concerning it is available. Insofar as is known, this is the only example of this type of deposit.

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PROSPECTING FOR BORON DEPOSITS

Several facts make the scientific prospecting for boron deposits feasible. First, boron is a very mobile element, having what has been described as a 'high migration capacity'; consequently it enters into solution in groundwater and forms secondary dispersion haloes or aureoles around deposits of boron, sometimes extending as much as 3·5 km from a deposit.[627,860,862,863] Secondly, boron is readily absorbed by growing plants. Third, a number of sensitive analytic methods and techniques have been developed for the determination of boron in small concentration.

The 'coefficient of migration capacity' of an element may be expressed as the ratio of the amount of that element to the amount of all other elements present in the same form in the same natural object. Boron in the soils of humid regions has a very high coefficient and permits the differentiation of borate and tourmaline dispersion haloes; in arid regions the interpretation is less clear.[645,862,863] The most distinct dispersion haloes are formed around datolite–danburite deposits.[627] The boron: bromine ratio may be of some significance.[626] Several analytic procedures have been developed for the study of these dispersion haloes.

Hydrogeochemical procedures are perhaps the most direct. Groundwater samples are obtained from various levels over an area, and the boron content and migration coefficient determined by any one of several sensitive analytical methods, usually colorimetric, sometimes spectrographic, atomic absorption, titrimetric, or other.[627,631,634,639,643,645,861,961,975]

Another method recently much in favour is that of neutron activation; in this procedure and its several variations a probe can be lowered into a borehole, or the recovered cores or other samples may be processed in the apparatus to determine the boron content.[358,624,625,632,637,638,640,642,858,865,877,915,988,1033,1052,1132]

In recent years it has been recognized that growing plants often take up trace elements found in the soil in which the plants are growing. Analysis of the plant foliage, particularly the leaves (where the boron concentrates) has made it possible to pinpoint likely areas to drill holes for further exploration.[646,859,862,1131,1196]

All of the above may be considered supplementary to the traditional geological formation correlation techniques long in use. A review of the basic methods for prospecting for boron has appeared.[647]

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SECTION A3

BORATE ORE DISCOVERY, MINING AND BENEFICIATION

BY K. J. MATTERSON

Introduction

Borax has been known for thousands of years; it was probably used by the Babylonians as a flux for welding gold jewellery, and the Egyptians are believed to have employed it for preserving their dead. Specimens of Chinese pottery utilizing colourful borax glazes made in the third century exist today. The ancient Persians and Arabians knew of borax, and the Arab word '*baurach*' appears in manuscripts written two thousand years ago. The Sanskrit word for borax was '*tincana*' and in Europe it was called *tincal*, a name which is still used for the mineral decahydrate borax.

Marco Polo brought borax crystals back from Mongolia in the thirteenth century, and thenceforth borax became a regular commodity in the overland caravan routes. Until the eighteenth century the ancient stagnant lake beds of Tibet supplied the borax demands of Europe and Asia, but in the middle of that century boric acid (*sassolite*) was found in hot springs or soffioni of Tuscany in Northern Italy. A century later borate deposits were found in South America (Chile) and later still in Turkey. It was not until the middle of the nineteenth century that borate ores were discovered in California, U.S.A., now the principal world source.

MINING

United States of America

In the U.S.A., the history of borate mining can be divided into four phases, starting with the finding of borax crystals in 1864 at the bottom of Borax Lake and Hachinhama Lake, Lake County, California.[1] (The first discovery in the U.S.A. had actually been by Dr John Veach in a mineral spring in Tehama County, California, in 1856.) Phase two began in 1872 with the recovery of ulexite and borax from playa surfaces in Eastern California and Nevada, resulting in the termination of the Lake County operations. The borate was mainly 'cottonball' ulexite (see Fig. 2(d), Section A1), found at Columbus Marsh and Teel's Marsh, Nevada. The laborious process of scraping up the borate mineral and refining it has been reviewed by Hanks.[1] Phase three dated from the discovery in 1882 of colemanite (see Fig. 2(a) and (b), Section A1) by prospectors employed by W. T. Coleman near Furnace Creek in Death Valley, near Lang in Los Angeles County, at Daggett in the Calico Mountains, and in the north-eastern part of Ventura County. Each of these deposits was mined by underground methods[2] and by 1907 they had almost replaced playa crust material as a source of borax. The fourth and final phase began in 1927 when the mining of borax from the Kramer deposit in Kern County, California, rendered the colemanite deposits uneconomic. In the same year, borax was first recovered from Owens Lake, California, and by 1931 was obtained in considerable quantities; production of borax at Searles Lake, California, had begun in 1919. The Kramer and Searles Lake deposits now constitute the major world source of borax.

Refs. p. 167. Literature coverage is up to 1973

Borates of the Kramer district were discovered accidentally in 1912 or 1913 by Dr J. K. Suckow when drilling a water hole, but it was not until 1925 that sodium borate was identified in a drill hole. The first shaft was sunk in 1926 and the ore mineral named *rasorite* after Clarence R. Rasor.[3] The mineral, sodium tetraborate tetrahydrate, was named *kernite* (after Kern County) (see Fig. 1(c), Section A1) independently by Dr Schaller, and the tetrahydrate bears this name today. ('*Rasorite*' is now the registered trade mark of U.S. Borax & Chemical Corporation for sodium borate concentrates.)

The United States is responsible for the bulk of the world's production of borates, which now come from the Kramer deposits and the brine at Searles Lake, together with minor quantities of calcium borate ores and ulexite (a mixed sodium–calcium borate, see Fig. 2(c) and (d), Section A1). Between the years 1864 and 1882 the annual production of borate minerals was < 3000 short tons, rising in the period 1882–97 to 8000 short tons. Production increased from 125,000 short tons in 1923 to 350,000 short tons in 1937[4], then rose progressively (with the exception of a wartime low in 1942) to a present annual level of over a million tons. (See Table I for production figures for boron minerals and compounds.)

Table I.—U.S. Boron Minerals and Compounds: Production Figures

Year	Sold or used by Producers (short tons)	B_2O_3 equivalent (short tons)	Value $	Reference
1937	358,898	—	7,232,897	12
1938	215,662	—	4,739,291	13
1939	245,284	81,800	5,689,797	13
1940	243,355	80,900	5,643,390	13
1941	301,282	95,200	6,785,662	13
1942	226,723*	77,600	5,733,648	13
1943	256,633	87,600	6,401,507	14
1944	277,586	91,700	6,579,587	14
1945	325,935	104,600	7,635,365	14
1946	430,689	129,800	9,575,866	15
1947	501,935	145,700	11,844,108	16
1948	450,930	134,700	11,147,735	17
1949	467,592	139,200	11,511,893	18
1950	647,735	191,000	15,890,000	19
1951	862,797	241,000	20,030,000	20
1952	583,828	169,100	14,105,000	20
1953	715,228	213,300	17,668,000	20
1954	790,449†	230,500	26,714,440	20
1955	924,496†	293,165	24,357,723	20
1956	544,677†	267,864	32,812,000	21
1957	541,124	269,251	38,041,000	21
1958	528,209	265,613	38,310,000	21
1959	619,946	314,286	46,150,000	21
1960	640,591	323,955	47,550,000	21
1961	603,000	313,000	46,936,000	22
1962	647,000	339,000	49,336,000	22
1963	700,000	369,000	54,981,000	22
1964	776,000	405,000	60,871,000	22
1965	807,000	425,000	64,180,000	22
1966	866,100	462,000	68,209,000	23
1967	892,000	473,000	69,819,000	23
1968	963,000	519,000	76,535,000	26
1969	1,020,000	551,000	81,261,000	26
1970	1,041,000	562,000	86,827,000	26
1971	1,047,000	568,000	89,856,000	26
1972	1,121,000	607,000	95,882,000	26

* Production reached a wartime low in 1942.
† Includes a higher proportion of crude ore to finished product.

By 1957, three mining companies accounted for practically all of the borates produced in California. The old Pacific Coast Borax Co., which merged with a potash company in 1956 to form the U.S. Borax & Chemical Corporation, operated mines in the Kramer District, Kern County, and extracted small quantities of colemanite near Shoshone and Ryan, Inyo County. American Potash & Chemical Corporation (now a division of the Kerr–McGee Corporation) and the West End Chemical Corporation (a division of Stauffer Chemical Company) produced borax as well as potash, sodium salts and other materials which are extracted from the complex brines of Searles Lake. At this time, the first-named company accounted for an estimated 78% of the U.S.A. borate production and the other two produced 25% and 5%, respectively. All three major producers are located in California; U.S. Borax & Chemical Corporation (a subsidiary of RTZ Borax Ltd.) now operate an open pit (*see* frontispiece) at Boron in the Mojave Desert, and the American Potash & Chemical Corporation and Stauffer Chemical Company still treat the brines at Searles Lake. Annual production capacities have recently been estimated, respectively, as 500,000, 100,000 and 25,000–30,000 short tons of B_2O_3.[26]

By far the most important borate source in the western world is the sodium tetraborate deposit in the Kramer area of California. The rich beds of relatively pure borax and kernite consist of a nearly flat-lying tabular mass, estimated to be 1½–2 miles (2·4–3·2 km) long and ½ mile (0·84 km) wide, and to have a maximum thickness of more than 200 ft (60·9 m). The massive borate body consists largely of borax, although kernite occurs in significant quantities and is mined along with it. Much of the borax is in the form of a crystalline mass, either transparent or clouded by included sediments. Some shale is present as interbedded seams or lenticular bodies as much as 2 in thick.[5] For the first 30 years after its discovery the deposit was worked by three separate mines, the Baker, the West Baker and the Jennifer. The mining method involved a conventional underground system of shafts, stopes and tunnels. A comprehensive account of underground borate mining in Kern County, California, was given by Obert and Long in 1952.[7] At that time it was economic to mine selectively, recovering only high-grade borax. The later post-war years, however, brought a sharp increase in the demand for borates, and for technical and economic reasons the underground selective mining technique was replaced by open-pit methods. Excavation of the initial pit began in 1956. In April 1957, the ore was uncovered, 137 ft (41·7 m) below the surface, after the removal of some 10 million tons of overburden (mostly gravel and shale). The initial pit, 200 ft (60·9 m) deep, 1400 ft (432·7 m) long and 1200 ft (364·7 m) wide, has undergone considerable expansion since (*see* frontispiece). The ore is mined by drilling and blasting the soft, thick benches. Before 1960 the ore was loaded into 100-ton dump trucks and hauled to the processing plant. Truck haulage to the surface was replaced in 1960 by an automatic ore conveyor at the 225 ft (68·5 m) level. The mined borax is crushed in two stages, effecting size reductions to 4 in and 8 in (101 mm and 203 mm) respectively, and then stockpiled prior to feeding to the refinery. The primary crusher is situated in the mine and feeds the conveyor.

The second major source of borates in the United States is in the brines of Searles and Owens Lakes. They are remnants of a drainage system which in Pleistocene times extended from the Sierra to Death Valley, California. Searles Lake is a vast flat, approximately 41 miles^2 (106·4 km^2) in area, above a permeable crystal body averaging 71 ft (21·6 m) thick. The margins of the 'lake' are covered by as much as 40 ft (12 m) of soft clay, but the centre 12-mile^2 (31 km^2) area is exposed. A second crystal body, discovered about 1946 and approximately 35 ft (10·6 m) thick, lies beneath the upper body and is separated from it by 10–15 ft (3–4·5 m) of impervious mud. The principal salts present are halite (NaCl), hanksite ($9Na_2SO_4,2Na_2CO_3,KCl$), trona ($Na_2CO_3,NaHCO_3,2H_2O$), and borax. The interstices of the crystal mass, amounting to about 50% of its volume, are filled with saturated brines that consist mainly of sodium chloride, potassium chloride, borax, sodium sulphate and sodium carbonate. The brines from the upper and lower crystal bodies are similar, but the proportions of dissolved salts vary.[5]

The average composition of brine filling the interstices of the crystal body in Searles Lake is given by Teeple[8] (Table II). Brine from the upper deposit contains 1·5–1·6% of borax and that of the lower deposit 1·9–2·0%. Borax is extracted from the upper brine[6] by concentration in triple-effect evaporators; the sodium salts crystallize and are removed and processed further. The remaining hot liquors, rich in borax and potash, are chilled, and the crystallized potassium chloride recovered. Agitation and seeding cause the borax to crystallize.[9] The lower brine is treated by a carbonation process in which carbon dioxide is bubbled through towers containing both upper and lower brines. Sodium bicarbonate crystallizes and is further processed to form soda ash. Borax is then obtained by chilling the carbonate-free brine. The American Potash and Chemical Corporation now operate a solvent extraction process at Trona, California, for the production of boric acid from low-grade, previously non-commercial, brines.[10] Brine feed containing about 1% of borate and about 35% of other dissolved salts is contacted by an organic polyol extractant. The extractant is selective to alkali borates, which are stripped from the extractant by treatment with dilute sulphuric acid to form boric acid and a mixture of sodium and potassium sulphates. The boric acid solution is then evaporated and crystallized, to form a high-purity product (see Section A7, 'Production of Boric Acids').

Table II.—Composition of Searles Lake Brine

Salt	Weight per cent
NaCl	16·5
Na_2SO_4	6·82
KCl	4·82
Na_2CO_3	4·80
$Na_2B_4O_7$	1·50
Na_3PO_4	0·155
NaBr	0·109
LiCl	0·021
Na_2S	0·020
As_2O_3	0·019
CaO	0·0022
Fe_2O_3 and Al_2O_3	0·0020
NH_3	0·0018
NaI	0·0014
Sb_2O_3	0·0006
Total solids	34·782

Owens Lake[5] before its desiccation contained carbonates, sulphates and chlorides; it now contains a crystal body similar to Searles Lake but having a maximum thickness of 9 ft (2·7 m). Both the crystal body and the brine are higher in soda content and lower in potash content than Searles Lake.

In 1957, H. S. Gale[5] estimated the Kramer deposit area to contain 92,250,000 tons of sodium borates, assuming the deposit is on average 75 ft (22·8 m) thick over an area of 500 (202 ha) acres. This estimate may be conservative. Turentine[5] estimated 25,000,000 short tons of borax to be present in the brines and salts of Searles Lake. This did not take into account the lower crystal body, and the upper body is now known to be larger than it was thought to be in 1926. Owens Lake contains an estimated 3,070,000 short tons of boron trioxide.[5] In 1952 S. H. Dolbear estimated that the ores of the Kramer deposit and the brines of Searles Lake and Owens Lake contained the equivalent of 15,000,000 short tons of boron trioxide. This is more than twice the total Californian production since 1864, when borate recovery began, and sufficient for approximately 50 years at the present rate of production. In 1958, a deposit estimated to contain 40 million short tons of colemanite was reported in Southern California.[11] The recently increased demand for colemanite for the manufacture of soda-free glass fibre has led other companies, especially oil companies, to

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seek the mineral and establish mines and associated upgrading facilities. Tenneco Oil Company has a deposit in the Furnace Creek district of Inyo County, California, but production has so far fallen short of the design capacity of 150,000 short tons of raw colemanite annually because of difficulties in calcining.[25–6]

Turkey

The earliest mention of Turkish borate deposits appeared in the literature in 1877[27] and referred to pandermite, although in 1865 a French company, Industrielle des Mazures, was operating the Aziziye mine near Susurluk.[28] These operations were later combined with those at the nearby Sultancayir mine, which had been operated since 1887 by the Pacific Borax and Redwood's Chemical Works Ltd., after 1896; in 1899 this company became Borax Consolidated Limited (now a subsidiary of RTZ Borax Ltd.).

All borate production prior to 1950 was of pandermite and by 1954 the reserves of the Sultancayir mine were almost exhausted and underground mining ceased. The Aziziye and Sultancayir mines were less than a mile apart and in the latter mine the conventional pillar-and-stall method of mining was used. Output between 1867 and 1914 was 233,000 short tons; between 1918 and 1937 it was 200,000 short tons and between 1938 and 1953 it was about 94,480 short tons. Output since 1953 has been as follows: 1954, 6989 short tons; 1955, 6633 short tons; 1956, an estimated 6800 short tons; and 1957, an estimated 9600 short tons. Since 1954, reported and estimated outputs related entirely to reworking of dumps.

In 1950 colemanite was identified by Husamettin Yakal[28] and this discovery resulted in a four-fold increase in total borate production from four mining companies: Mortas, Rasih ve Ihsan, Yakal and Sayakci Sirketleri, which altogether operated approximately twelve mines in the Bigadic area of north-western Turkey.

Marketing difficulties in Europe limited production at this time to about 30,000–32,000 short tons per annum.[28] The main minerals encountered in 1950 and later in this new development area were colemanite ($2CaO,3B_2O_3,5H_2O$) and ulexite ($Na_2O,$-$2CaO,5B_2O_3,16H_2O$). Other hydrated borates containing calcium, or calcium with magnesium or silicon, which were also discovered included meyerhofferite, inyoite, priceite, terschite, hydroboracite and howlite.

The Yakal group of mines produced 2000 short tons in 1951 and 1952. This output increased to 2500 short tons in 1953, 6000 short tons in 1954 and 11,000 in 1955. In 1956 the output was reduced to 8000 short tons owing to marketing problems. The main mine of the Yakal group was the Gunevi mine, where both colemanite and ulexite were mined by drilling and blasting. Only 20% of the production required hand trimming to remove the clay, and it was readily possible to separate the colemanite from the ulexite by selective mining and hand picking. This was the only mine in the Bigadic area where explosives were used. Other mines in the Yakal group were at Kurt Pinari, Kireclick, Acep, Tuglu Degirman, Borekci and Domuz. The most difficult mining problem encountered in the Bigadic district was the support of the workings. In 1955, the Yakal group used 0·404 m^3 of timber per ton of ore mined.

Bortas and its parent Mortas entered the borate mining business shortly after the discovery of colemanite in the Bigadic district in 1950 and operated mines at Begendikler, Yenikoy, Utzitler, Killik, Gocenoluk, Kirka, Sindirgi, Kestelek, Kucukler and Espey, which aggregated an average of 15,000 short tons output per year between 1955 and 1958.

The Espey mine, which started production in September 1957, by 1958 was producing 35 short tons of ore per day. Other borate mines in the Bigadic area were Ankara 2 and 3 (operated by Rasih ve Ihsan Maden); the total output in 1957 was 4000 short tons and ore reserves were estimated at 80,000 short tons. The Ali Sayakci mine, north-west of Bigadic, had an output of 10 tons per day in 1956 with reserves estimated at 60,000 short tons proven and 250,000 probable.

By the early 1960s[33] approximately 25 mines had been opened in eight locations in Western Turkey. As there were no treatment plants in Turkey at that time the crude ore was exported as a raw material. The mines were operated by four private mining companies and one State-owned company with daily production varying from 10 to 200 short tons. Beneficiation of the colemanite ore was effected by hand picking following selective mining to produce a shipping grade ore containing about 43% B_2O_3. The exported mineral was shipped from Bandirma and Derince on the Sea of Marmara at the rate of 70,000 short tons per year.

In 1963 a new company, formed by American Potash and Chemical Corporation and Fethiye Mining Company, bought the Tuglu mine near Bigadic[37] to supply colemanite ore for a new boric acid plant owned jointly by the American Potash and Chemical Corporation and Ugine-Kuhlmann. In 1964[38] the State-owned mining company Etibank announced that the expected completion date of their boric acid and borax plant would be two years later. Etibank's Hisarcik mine was to supply the plant with colemanite by rail.

During 1964, Turk Boraks Medeneilik, originally formed in 1955 as a subsidiary of Borax (Holdings) Limited, now RTZ Borax Limited, and who had been actively exploring for several years[35], developed a sizeable colemanite deposit near Kirka; the company was reported to have discovered a sodium borate deposit[35,41] about 164 ft (50 m) thick and of great lateral extent, and proved the existence of 40 million tonnes of borate mineral. The sequence of borate formation in this deposit was later investigated by Inan *et al.*[39–40]

The annual production of borate minerals in Turkey from 1924 to 1971 is shown in Table III. Etibank's Hisarcik mine was the major producer in 1964[35] with 51,000 tonnes. The Bortas–Mortas group produced 40,000 tonnes from their Espey and Killik Mines near Emet. Production of minerals reached a record 225,266 tonnes in 1966[36], an increase of 31% in comparison with 170,977 tonnes in 1965. The then rapidly increasing demand for colemanite was partly due to its use in glass fibre manufacture. The largest producer in 1966 was Etibank's Hisarcik mine with 92,000 tonnes, some of which was stockpiled since it contained iron and arsenic impurities. Other principal operators including Turk Boraks (who were then operating the

Table III.—Annual Production of Borate Minerals in Turkey

Year	Tonnes	Reference	Year	Tonnes	Reference
1924	11,000	25	1949	7,082	28
1925	16,051	25	1950	9,764	28
1926	15,574	25	1951	12,051	28
1927	17,881	25	1952	13,730	28
1928	14,943	25	1953	6,436	28
1929	13,528	25	1954	14,331	28
1930	5,456	25	1955	42,186	28
1931	6,501	25	1956	29,300	28
1932	4,994	25	1957	27,378	29
1933	7,553	25	1958	69,402	29
1934	7,517	25	1959	43,336	29
1935	5,082	25	1960	71,027	29
1936	6,484	25	1961	88,615	29
1937	4,664	25	1962	113,941	30
1938	4,064	25	1963	88,088	30
1939	15,170	25	1964	128,254	30
1940	5,018	25	1965	170,977	31
1941	5,038	25	1966	225,286	31
1945	5,034	28	1967	228,500	32
1946	2,210	28	1968	265,883	45
1947	3,608	28	1969	323,470	45
1948	5,314	28	1971	570,503	26

Table IV.—Exports of Boron Minerals from Turkey (tonnes)

Reference	34	34	34	34	34	35	35	35	36	36	44	43
Year	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
Country of destination:												
France	3,754	7,070	6,599	4,622	18,000	—	—	31,000	31,470	39,676	49,985	—
E. Germany	—	—	—	—	—	—	—	2,000	8,000	—	—	—
Italy	4,010	5,171	12,564	22,813	27,450	—	—	45,722	60,454	57,480	63,627	—
Poland	—	2,400	4,600	2,000	6,500	—	—	7,500	7,500	10,650	11,750	—
U.K.	3,150	3,993	3,401	4,250	7,300	—	—	5,590	15,319	11,288	10,935	—
U.S.A.	4,572	21,916	21,262	25,128	2,400	—	—	528	8,608	19,054	21,559	—
Others	6,508	10,712	13,070	2,710	5,440	—	—	26,094	21,218	37,177	53,476	—
Total	21,994	51,262	61,496	61,523	67,090	80,480	91,540	118,434	152,569	175,325	211,332	231,954

Espey and Killik mines) and Rasih ve Ihsan produced 126,282 tonnes and sold 115,456 tonnes.

The production of boron minerals in 1967[44] reached 228,500 tonnes; exports also increased and represented Turkey's third most important foreign exchange earner. Production at Etibank's Hisarcik mine fell from 99,180 tonnes in 1966 to 76,000 tonnes in 1967. Etibank's boric acid plant was reported to be on stream in November 1967, using domestic colemanite and imported sulphuric acid.[44] In 1968, the production of boron minerals[45] rose to 265,883 tonnes, and in 1969 to 323,470[45], an increase of 22% over the 1968 figure.

In 1969 a Government committee estimated the Turkish sodium borate reserves to be 400 million tonnes and recommended nationalization, not only of these deposits, but of the whole boron industry.[46–8] 570,503 tonnes of crude product, virtually all of which was colemanite, was produced in 1971.[26] The exports of boron minerals from Turkey for 1957–68 are given in Table IV and show a large and increasing amount of minerals exported to France and Italy.

Proven and probable reserves of boron minerals[29] in western Turkey are of the order of tens of millions of tonnes, but the potential could be higher on the basis of the indicated geology and the extent of the deposits. In 1968 Etibank and the Mining Prospecting Institute planned to make a prospecting survey in the area of Kirka and Seyitgazi (Eskisehir Province) to determine the resources of borax in the area.[42]

Argentina and Chile

In 1968 Argentina was reported to occupy the third place among the free-world producers of borates.[49] The largest producer, Boroquimica SAMICAF (a subsidiary of RTZ Borax Ltd., London) operate an open-pit borax mine for the production of refined and anhydrous borax at Salta. The refining plant is 248 miles (400 km) from the deposit, which is located approximately 13,451 ft (4100 m) above sea level at Tincalayu in the Andes. The absence of a readily available water supply, the altitude and the temperature variation make the establishment of a plant near the deposit economically difficult. Other borate minerals occur in Argentina, notably ulexite (which is mined), hydroboracite, colemanite and inyoite (which are not mined at present). Other minor deposits of borax also occur in the Salta/Catamarca provinces of northern Argentina and have been worked from time to time.

The production of borate minerals in Argentina from 1955 to 1969 is given in Table V. In the years 1968–69 approximately 7000–8000 tonnes were exported to Brazil and a smaller quantity (300–400 tonnes) to Uruguay.[52]

Table V.—Production of Borate Minerals in Argentina

Year	Ulexite (tonnes)	Borax (tonnes)	Total borate (tonnes)	Reference
1955	13,000	23,000		50
1956	20,000	<25,000		50
1957		36,000		50
1964			12,000	51
1968			21,026	52
1969			29,154	52
1972			50,000	26

In 1962, Borax (Holdings) Ltd. (London) were reported as being the only borate producer in Chile, operating a ulexite mine at Ascotan in western Antofagasta Province, near the Bolivian border. Chile had been a producer and exporter of ulexite since the last century but production dropped from 5756 tonnes of sun-dried ulexite in 1959 to 2919 tonnes in 1960. The mine closed down in 1961 owing to high stocks and was expected to reopen in 1962 after the recession in the glass and ceramic industries in Chile.[53] The mine did reopen in 1962[54], but production began to decline again from 1966, the mine closing finally in 1967 after achieving an annual production of approximately 4000 tonnes, and sufficient stocks for several years.[49]

Production figures for the years 1959–66 are given in Table VI. In 1957 borate reserves in Chile were estimated at 20 million tonnes.[5]

Table VI.—Production of Borate Minerals in Chile (tonnes)

Year	Ulexite (33% B_2O_3)	Reference
1959	5756	54
1960	2919	54
1961	160	54
1962	3814	55
1963	2981	55
1964	3300	56
1965	4600	57
1966	400	49

U.S.S.R., Eastern Europe and China

Hydroboracite was discovered, and so named, in the Caucasus area in 1933. The joint discovery of potash and boron mineralization in the salt dome at Lake Inder[49] led in the following year to widespread prospecting in the Caspian Sea area.[58] Borate deposits were discovered in Kazakhstan (Soviet Far East), and contact-metosomatic (skarn) deposits containing boron silicates (datolites, danburites) and borates (kotoite, suanite, ascharite) were found at a number of locations in the Far East, Siberia, Central Asia and Caucasus.[49, 59–60] Deposits of ludwigite in association with magnetite were reported in the Lake Baykal area[60], and the Soviet minerals industry was stated to have vast reserves of boron minerals.[59]

Boron-bearing saline lakes and small playas (with ulexite) are located in a number of areas, and several groups of mud volcanoes producing boric acid are also known, particularly at Kerch-Taman in the Crimea and near Baku.[58] Other boron-containing brines and sediments have been discovered in other parts of the U.S.S.R., but none appears to show an exploitable potential.

The most abundant ore types are hydroboracite–ascharite minerals occurring in the Caspian Sea area. Grades vary from 1·5 to 25% B_2O_3 and they usually occur with other borates (colemanite, inyoite, ulexite, boracite) and gangue minerals (halite, gypsum/anhydrite). Concentrates containing 44% B_2O_3 are obtained by crushing and then removing the halite gangue by washing or leaching. The mineral associated with clay and gypsum/anhydrite is upgraded to 18–20% B_2O_3 (and occasionally to 34% B_2O_3) by physical beneficiation.[58] Datolite ores containing 3–15% B_2O_3 are upgraded to 16% B_2O_3 by physical methods and flotation; low-grade ores are acid-leached to extract the boric oxide values.[58] Ludwigite-type ores contain approximately 4% B_2O_3 and can be upgraded to as high as 10% B_2O_3 as a by-product from the separation of magnetite. The boron values are then extracted by sintering with limestone, followed by acid leaching.

Early efforts to recover borax from mud volcanoes of Kerch, Taman and Baku were abandoned in 1942. Continued expansion of both open-pit and underground mining is referred to in the literature of the 1960s and it seems probable that the Chalker deposits (north of Inder) have also been exploited.[58]

The U.S.S.R. estimated production of boron minerals and compounds, according to V. V. Strishkov[49] was as follows (tonnes B_2O_3): 1964, 64,000; 1965, 65,000; 1966, 67,000; 1967, 68,000.

It was reported[61] in 1970 that exports of chemicals (including borax and boric acid) from Kazakhstan rose by 25% over 1969 exports. The All-Union Export–Import Agency, Dalintorg, sells boric acid and calcium borate to Japan, and hopes to increase this trade by selling datolite and danburite concentrates mined in the Soviet Far East and Eastern Siberia. In 1972, Dalintorg[62] advertised datolite concentrate (16% B_2O_3 min., 2% Fe_2O_3 max.), available packaged or in bulk for export to Japan, other S.E. Asian countries and Australia.

A molten anhydrous borax plant, operating in the mining and chemical complex in the maritime territory of the Soviet Far East, was reported in late 1972.[63] The ore for this plant is mined in the Sikhote–Alin mountains. It was also reported that a plant producing enamel frits would soon be operating in this complex.

China has developed its own primary boron products industry since 1956. The only sources revealed are a number of semi-dry playa lakes in south central China[49] and northern Tiber.[58] In only one of these, the Iksaydam dried lake area in the Tsaidam Basin in Chinghai (Tsinghai) Province, reportedly quite large in area, have borates become a significant product.[26] The borax is believed to be derived from brine in the lake as a by-product in potash extraction.[58]

BENEFICIATION

The western world is considerably more fortunate than the eastern world in that large deposits of high-grade sodium and calcium borates are known there and are exploited. Consequently, upgrading processes (in the West) tend to be less sophisticated than methods which must be used by the eastern bloc countries, or methods used to upgrade minerals of other elements which occur in a less pure form. In the eastern world, high-grade borate mineral deposits are rare, the boron value usually occurring as a complex borate (e.g., borosilicate) and being therefore more difficult to win. Since elemental boron does not occur free in nature, the boric oxide content of the ore or mineral is used to describe its value; borax contains approximately 36% B_2O_3 and colemanite approximately 50% B_2O_3. Many of the conventional methods of mineral processing or upgrading have been applied to boron minerals in order to secure the highest possible boric oxide value for the concentrate, which may then be sold directly or fed into a plant for borax, anhydrous borax, sodium perborate, boric acid or boric oxide production. These methods are discussed in the following sections.

Calcination

Interest in the beneficiation of borate minerals by calcining has been shown since 1920. Most borate minerals contain some molecules of water of crystallization (borax contains 10, colemanite 5, inyoite 13 and ulexite 16, for example) and it is possible to increase the boric oxide value of the ore simply by the removal of all or part of the water of crystallization present in the mineral. There are however, further advantages of the mineral colemanite in that calcination is accompanied by decrepitation and, depending on the conditions of calcining, the massive colemanite can be reduced to a powder without prior crushing (often leaving gangue as coarser material which can be removed by screening). Other borates do not decrepitate on calcining (despite the claims of at least one patent[64]), but since water is lost, the bulk density of the mineral is reduced. In some cases, particularly that of borax, a 'puffed' material of varying specific gravity can be produced according to the conditions of drying or calcining. The specific gravity differential induced by calcination can then be used as a basis for further upgrading techniques. In 1924, Rasor[65] separated colemanite from its associated gangue by calcining the ore to produce a difference in specific gravity between the borate and the gangue, and separated the latter from the decrepitated colemanite by screening and discarding the oversize. The fine colemanite was then separated from the fine gangue by pneumatic classification. In 1937, Corkhill[66] recommended an inclined calciner approximately 80 ft (24·3 m) long and 6 ft (1·8 m) in diameter rotating at a speed of 4 r.p.m., with a 30-min residence time, for removing five of the ten molecules of water of crystallization in borax. The drier was heated by hot air or gas from a fuel-oil burner. The drying of borax under these conditions was achieved without 'puffing', reduced the specific gravity of the feed material from 0·730 to 0·666 and increased the boric oxide content from 36 to 48%. The process was also claimed to be applicable to colemanite, ulexite and rasorite, but no examples were given. In 1946, Handel[67] described improvements for the production of calcined or anhydrous borax. The powdered borax fell from a sieve down an 85-ft (30 m) vertical kiln, of 3 ft 6 in (1 m) diameter, heated to 600–700°C by hot gases introduced tangentially into the base of the vertical furnace. A scraper removed the molten glass or dehydrated powder, whilst an efficient dust collector was used to remove anhydrous borax powder from the spent gas stream. Harman[68] in 1957 described a process of extracting boron values from colemanite which involved moistening the ore with approximately 25% of water, followed by calcination at temperatures between 300 and 2000°F. The decomposition is claimed to be improved by the addition of an acidic oxide (silica, for example). Boric acid or boric anhydride was produced directly as white fumes, which were condensed and collected. In 1966, Plystevskii *et al.*[70] described the calcination of datolite at 950–980°C yielding CaO,B_2O_3, β-CaO,SiO_2, α-quartz and cristobalite. The product, calcined datolite, can be used as a boron fertilizer, as it contains boron soluble in carbonate-containing media. Shishko and Shabalin[71] described the kiln used for the process, which proceeds according to the equation:

$$2CaO,B_2O_3,2SiO_2 \rightarrow CaO,SiO_2 + CaO,B_2O_3 + SiO_2$$

The parameters of the calcination are given.

In 1963, Griswold[64] described a method of calcining and classifying minerals, particularly those which decrepitate at a temperature below their melting point. He claimed that borax decrepitated at 200°C, tincalconite at 130°C and colemanite at 350°C and stated his process to be suitable for all three minerals. In fact, borax and tincalconite do *not* decrepitate but lose water of crystallization and reduce their specific gravities significantly, according to the conditions of the drying or calcination. Griswold claimed a process of simultaneous decrepitation and classification accomplished by roasting in a fluid-bed apparatus such that the decrepitated borate is removed from the fluid-bed roaster. In commercial application this process was described as an 8 ft (2·4 m) diameter fluidized-bed reactor operating at a temperature of about 550°C. Colemanite ($-\frac{1}{2}$ in) feed was fed into the furnace at the rate of 20 t h^{-1}. Boric oxide recoveries in the exhaust gases were claimed to be 75–80%. Colemanite calcination in a rotary kiln was described in a recent patent.[69]

In 1970, Solvay et Cie[72] took advantage of the inaccuracy of description and claims in the Griswold patent[64] and described a similar process for the enrichment of 'non-decrepitable' borate minerals such as borax. Again a simultaneous decrease in specific gravity and classification was claimed for a fluidized-bed system operating at temperatures between 110 and 700°C. After expansion of the borax, the bulk density was reduced to 0·025 from 0·785. (See also under 'Preparation and Production of Alkali–Metal Borates', Section A10.)

Flotation

Flotation of boric acid and borax was first described by Andreeva and Kuzin[73] in 1937 when mixtures of boric acid and Epsom salt ($MgSO_4,7H_2O$) were separated by flotation after treatment of the Inder boracite. Sodium chloride was used in the above separation with approximately 1·5% boric acid in the tailings. The purity of the boric acid concentrate was found to depend on the crystalline condition of the boric acid and amount of magnesium sulphate mineral inclusions in it. Boric acid was also separated from a mixture of boric acid, magnesium sulphate and magnesium sulphite without the use of a flotation reagent, in good yield, after treatment of the boracite with sulphur dioxide. Borax and sodium sulphate decahydrate (Glauber's salt) were also separated by flotation using 'acid oil' and lead nitrate but considerable quantities of reagents were used. The addition of sulphuric acid simplifies the problem considerably. Knickerbocker and Shelton[74] examined the feasibility of the treatment of boron minerals with sulphur dioxide in solution or with sulphuric acid and floating the boric acid formed from the gangue. Boric acid is a natural 'floater' from solution, but it was found that gangue depressants gave a cleaner concentrate. A colemanite ore assaying 20% B_2O_3 gave a greater than 90% recovery with a product better than 90% pure. Wiseman[75] described a similar method (but without flotation) for processing a colemanite slurry containing a controlled concentration of a water-soluble salt of an alkaline-earth metal (calcium chloride). Practically complete recovery of boric oxide was obtained when a colemanite slurry with added calcium chloride was treated with sulphur dioxide at 70°C until a pH of 4·5 was reached. The boric acid solution containing calcium chloride was separated from the calcium sulphite ($CaSO_3,2H_2O$) sludge, the boric acid crystallized out, and the calcium chloride mother-liquor returned to the reaction step. Knickerbocker, Fox and Yerkes[76] calcined a 17% B_2O_3 colemanite ore which, after screening, gave a concentrate containing $>40\%$ B_2O_3 and when leached with carbonic acid gave a 99% boric oxide recovery. The calcium borate was recovered by precipitating with lime. No troublesome impurities were found to accumulate in the leach circuit, and the product assayed B_2O_3 53·31, SiO_2 0·32, Al_2O_3 0·15, Fe_2O_3 0·15, CaO 41·23, MgO 0·80, CO_2 0·29, and SO_3 1·5%. In 1954, Klassen and Ratobyl'skya[77] improved the flotation characteristics of hydroboracite by the addition of turpentine or emulsified non-polar reagents (kerosine). A higher extraction rate was obtained and a higher boric oxide value in the concentrate was achieved owing to the increase in hydrophobic properties of the hydroboracite surfaces. The influence of alkali (sodium hydroxide) and sodium carbonate addition on the flotation of hydroboracite was later investigated by Borisov.[78] The 'electrokinetic index' was observed for many minerals, and it was observed that the addition of sodium carbonate solutions had a greater effect on the electrical double-layer structure on the surface of minerals than sodium hydroxide solutions. In 1963[79] Giatsintova *et al.* investigated the effect of bubble age on the time of its adhesion to surfaces of minerals (including datolite and danburite). The effect was related to surface tension measurements in the presence of various surfactants. Similar studies by Solozhenkin and Urman[80] used N.M.R. methods to investigate the interaction of flotation reagents with minerals. N.M.R. measurements showed danburite surfaces to form a strong bond with water, indicating reduced mobility, and this explains why large amounts of oleic acid are required for its flotation. The use of wetting agents in flotation was also reviewed by Dean, Clemmer and Cooke[81] with reference to borates and other minerals. Kuzin[83] investigated the separation of alkali sulphates and their double salts with nitrates and borates from other alkali and alkaline-earth salts by flotation. The reagents used were sulphuric acid esters and sulphonic acids of aliphatic and naphthenic hydrocarbons containing four or more carbon atoms. More recently, Russian workers have studied the preparation of boric acid from magnesium ores and datolite, and certain economic advantages over established techniques were claimed.[82]

Boron Values from Brines

Solution mining of soluble salts serves the dual purpose of mining and upgrading processes in one step, but technical and economic problems also limit the usefulness of such an operation. During the development of the Kramer deposit in the Mojave desert, California, U.S.A., consideration was given to solution mining, and it was actually tried on a small scale in order to improve the recoveries of conventional underground mining methods.[84] Ultimately the idea was rejected and open-pit mining methods were adopted. Edmonds *et al.*[85] described a method of *in situ* mining for several soluble salts, including borax, in which a non-solvent liquid having a specific gravity of less than 1·0 (e.g. mineral oil) was introduced into the cavity, forming a protective layer on the floor of the cavity. Blumenberg[86] described a method for recovering insoluble calcium borates by introducing a hot calcium chloride solution into the deposit, removing the resulting magma, and cooling to cause precipitation of a proportion of the dissolved calcium borate minerals. Another patent[87] specifies the use of hot ammonium chloride solution in place of the calcium chloride solution.

The sea undoubtedly represents the largest virtually untapped source of minerals available to man. Boron is present in sea water to an average value of 4·6 p.p.m.[88, 89] On the other hand, Hess[90] claims an average value of 0·029 weight per cent of boron in the Pacific Ocean based on 54 samples), and 0·03 weight per cent, present in the Atlantic Ocean (based on four samples). Hanson and Murthy[88] calculated that the probable effluent from a 50-million-gallon-per-day large-scale desalination plant using sea water would contain 13·8 p.p.m. of boron, representing an annual throughput of 4840 tons of borax. They also showed that the probable economic breakeven concentrations for treating the effluent from such a plant would be 22 p.p.m. boron in U.K., 64 p.p.m. boron in U.S. and 15 p.p.m. boron in India.

Boron exists in the sea as boric acid, the borate ion and the $B(OH)_4^-$ ion[91], and during the process of evaporation of sea water the major part of the boron remains in solution. Boron is reported to be co-precipitated with magnesium from sea water[92–3], the proportion of the contained borate precipitated reaching a maximum of 90% at a pH of 10–10·8. A Japanese patent[94] recommends treatment of sea water with 20% sodium hydroxide solution to precipitate magnesium and boron at a pH of 10·0. Sulphur dioxide is bubbled through the resulting magnesium hydroxide slurry to a pH of 8·5 to isolate the boron. Boron recoveries of up to 85% have been attained by this means. Shoikhet *et al.* used calcined brucite marble as a sorbent containing active magnesium oxide[95] suitable for the recovery of boron values from natural waters.

Many processes have been suggested and used for the recovery of boron values from natural brines. The patented American Potash and Chemical Corporation's solvent extraction process has already been mentioned.[96] Data on solvents, distribution coefficients and solvent losses are given in the patents[97–9], and Klopfenstein and Arnold[100] have described the commercial process. Other water-immiscible organic liquids containing one or more aliphatic vicinal diols and alkyl-, alkoxy- or halogen-substituted catechols have also been proposed as solvents.[101] Other solvents such as isobutyl alcohol, isoamyl alcohol or benzyl alcohol and a frothing agent are reported to give a 41% boron recovery in a single contacting stage.[102] Similarly, isoamyl alcohol[103] was reported to be the best solvent for extracting boric acid from solutions containing magnesium chloride and boric acid. The use of ion-exchange techniques for the removal of boric acid from brines has also received a great deal of attention. A boron-specific ion-exchange resin based on *n*-methyl glucamine has been reported.[104] The recovery of boric acid from brines available in Italy was investigated by Nencetti and Tartanelli[105] using anion-exchange resins and the development of a boron-specific ion-exchange resin, 'Amberlite IRA–140', was also reported.[106] Nikol'skii *et al.*[107] investigated the adsorption of boron on a number of anion-exchange resins and selective absorbents under static and dynamic conditions. Extraction yields of 90–100% for boron were obtained with certain resins from natural waters under favourable conditions. Almassy *et al.*[108] demonstrated the possibility of processing hard ores with acidic resins and a small amount of inorganic salt as catalyst. Optimum 94% boric acid yields were obtained by using ascharite ore and resin ('Dowex 50' or SD–8–SO_3H) at 70–80°C after 1·5 hours of stirring.

Magnetic and Electrostatic Separation

Magnetic separation has been used to some extent for the beneficiation of boron-containing minerals. F. W. Corkhill[109–11] described the treatment of borax-type minerals, which are subjected to progressive magnetic separation and afterwards calcined at 100–125°C to give a product which is stable in air. Ramsey and Brier[112] discussed the fundamental principles and commercial applications of high-intensity magnetic separation with reference to several minerals, including borax. Also, Johnson[113] described the operative details of equipment for the magnetic separation of borax. This process was used at Boron in California, U.S.A., by the U.S. Borax Corporation prior to the changeover from conventional underground mining to open-pit methods. Two coarse ore products (one of $\frac{1}{8}$ in largest size and one of $\frac{1}{16}$ in largest size) from the fine crushing plant were fed at constant rates to the magnetic separators. The high-intensity machines exploited a small magnetic property in the clay. A portion of the concentrate was sold directly; the greater part was calcined to remove five of the ten molecules of water of crystallization, and a small proportion was calcined to remove substantially all the water of crystallization from the borax. The magnetic separation process was discontinued after the change to open-pit mining and the building of the new plant.

Fraas and Ralston[114] described an apparatus used for separating ulexite (pretreated with benzoic acid) and bentonite. The apparatus separated electrostatically charged particles after charging by intimate contact on horizontal vibrating plates. Plates of copper sulphide and celluloid were used for the separation, and the accumulated charges on the non-conductive plates were dissipated by heated alkali-oxide-coated platinum wires suspended above the plates.

Miscellaneous Methods

Other methods for the beneficiation of borate minerals can be classified in three groups: (i) leaching, (ii) scrubbing, and (iii) methods involving dissolution in acid, or reaction with sodium carbonate and bicarbonate.

In the first group, boron values were recovered from calcium borate ores by May and Levashaff[115] by leaching with a hot aqueous solution of ammonia and a hot aqueous solution of carbon dioxide at temperatures greater than 83°C. Soluble ammonium borate, $(NH_4)_4B_6O_{11}$, and solid calcium carbonate were formed. After filtration the ammonium borate was crystallized and calcined, allowing the ammonia to be recycled. The carbon dioxide was also regenerated by calcination of the ore and the calcium carbonate. In 1943 Nagai[116] produced boric acid by leaching kotoite with hydrochloric acid to remove calcium and magnesium carbonates. The same mineral after calcination was also heated with sodium carbonate solution in an autoclave at 153–180°C when 80–85% of the total boric oxide was converted into the sodium salt.[116] A novel method for the treatment of a borate ore containing the difficultly soluble mineral kernite was patented in 1928 by Blumenberg.[117] The patent proposed treating the ore with sodium carbonate solution *in situ* to convert the kernite into the easily soluble sodium metaborate, which could be dissolved and removed from the deposit. A practical difficulty with this process for borax production would be to readjust the $Na_2O:B_2O_3$ molecular ratio of the metaborate (1:1) back to that of borax (1:2). Also, since borax and kernite usually occur in the same mineral deposit it would be difficult to operate solution and conventional mining methods in the same mine.

Methods of beneficiation by scrubbing or attrition were reported by Batuner[118] and Connell and Rasor.[119] Batuner carried out the scrubbing of the ore in a multistage series of agitators and settling chambers. Connell and Rasor upgraded colemanite, tincal and ulexite ores by scrubbing in a saturated solution of the mineral in the presence of yieldable surface-attrition devices such as rubber balls. The solid borates were then separated from the slimes produced.

Acid leaching, dissolving or other methods of beneficiation are tantamount to actual boric acid or borax processing and as such are fully discussed elsewhere. However, a few methods are worthy of mention. The preparation of borax by the solid-state reaction of natural and calcined colemanite or priceite with a mixture of sodium bicarbonate and carbonate was investigated by Alpar and Gulensoy.[120] Maximum yields of borax were obtained at 200–300°F with the calcined mineral. In the manufacture of boric acid from kernite containing magnesium as an impurity, Franke[121] patented a method for treating the ore with hot sulphuric acid to form a solution containing boric acid with magnesium and sodium sulphates. The solution was cooled to crystallize a crop of boric acid. The resulting liquor was then concentrated to the point of saturation with respect to sodium sulphate, when sodium magnesium sulphate and further quantities of sulphate-free boric acid were crystallized sequentially. Dwyer[122] proposed the extraction of boron values from a calcium borate ore by reacting the ore with ammonium sulphate solution at 95–105°C to form the soluble ammonium borate. The calcium sulphate and gangue were removed by filtration and the ammonium pentaborate recovered by crystallization from the solution. The pentaborate was then converted into boric acid by reaction with sulphuric acid or ammonium hydrogen sulphate, or converted into methyl borate and either distilled to obtain the methanol–methyl borate azeotrope or acid-hydrolysed to form boric acid directly. May and Levascheff[123] examined the extraction of boric acid from colemanite by digesting the ore with hydrochloric acid; the extraction of boron values from datolite was investigated by Nikolaev and Bogatyrex.[124] They found that up to 95% of the boron can be recovered from datolite by dissolving the mineral in 52% sulphuric acid or 7% hydrochloric acid and recovering the boron as methyl borate. In 1972, Mathis[125] described a process for producing a clear solution of calcium borate in boric acid solution from a low-grade calcium borate ore which does not contain appreciable quantities of sodium borate. In an example given, 53 g of colemanite (45% B_2O_3) were dissolved (97% efficiency) in 20 min at 90% in a boric acid solution, increasing its boric oxide content from 109 to 118 g of B_2O_3 per kg. A further process for the recovery of boron values from an insoluble borate ore is described in a Belgian patent[126]; calcium and magnesium borates are rendered water-soluble by contacting an aqueous slurry of the ore with a sufficient amount of carbon dioxide to precipitate the calcium and magnesium carbonates, the boron values remaining in solution.

Various methods for the extraction of boron values from tourmaline were described by Stoicovici *et al.*[127] and the decomposition temperature of the mineral was investigated by Henderson.[128] Henderson reported that a higher rate of extraction of boron values was obtained when leaching from tourmaline decomposed under reducing conditions, rather than from tourmaline decomposed in air. Kamiko[129] extracted boron values from tourmaline by heating with sodium carbonate at 780–850°C for 30 min and extracting the borax by leaching with hot water, which gave a 95% recovery.

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SECTION A4

BORIC OXIDE

(BORON TRIOXIDE, BORIC ANHYDRIDE, BORIA)

BY J. DULAT

The popularity of the alternative names 'boron trioxide' and 'boric anhydride' has declined and the use of 'boric oxide' is now preferred. The name 'bora' suggested for the oxide in 1935[1] has not found acceptance, but the version 'boria' is fairly often used, particularly in the catalysis field. The commercial product is also known as 'anhydrous boric acid'.

FORMATION

Boric oxide is a product of a variety of reactions (Mellor, V, 41) some of which deserve further comment. The product obtained on combustion of elemental boron in oxygen is usually contaminated with boron, and possibly boron suboxides, because the surface layer of the molten boric oxide first formed wets the unreacted solid and shields it from contact with the oxygen.[2] Since the rate of oxidation is thus dependent principally on the remaining amount of exposed unreacted solid, it diminishes with time according to a parabolic law[3], and is not markedly affected by moderate variations in oxygen gas pressure. The rate of reaction is, however, increased and the temperature of ignition lowered considerably in the presence of fluoride and silicofluoride impurities.[4] The presence of combustible organic materials, e.g. benzoic acid, facilitates contact between the reactants, but even with the use of such aids it is difficult to achieve a complete reaction.[5–7]

In the preparation of boron carbide from a mixture of boron trichloride, carbon monoxide and hydrogen, the appearance of boric oxide alongside the carbide was attributed to the reaction[8]:

$$14B + 3CO = B_2O_3 + 3B_4C$$

and if this is correct, boron carbide would be found among other contaminants in boric oxide prepared in the presence of organic matter. In one specific instance the presence of the carbide could not be confirmed in a product obtained by combustion of boron in oxygen at 28 atm pressure in the presence of carbon black[2], so that some doubt remains as to the identity of contaminants in boric oxide obtained by combustion methods. The presence of the contaminants can usually be demonstrated by their insolubility in water.

The formation of boric oxide in the combustion of liquid or volatile organoboron compounds, as in the reaction:

$$(CH_3O)_3B + O_2 \rightarrow B_2O_3$$

has a number of practical applications, e.g. in gas welding (*vide infra*), but sometimes it may be troublesome, e.g. in the combustion of high energy boron fuels.[9] The growth of droplets of liquid boric oxide in flames can be studied using light-scattering techniques.[10]

PREPARATION

Vitreous Boric Oxide

Boric oxide glass is usually prepared from boric acid by dehydration. The product is colourless, hard and tough. Various methods have been proposed for obtaining the material in a form which is easier to break and grind. Careful drying of boric acid at 200°C in vacuum and over phosphorus pentoxide gives a slightly sintered or porous material.[11,12] An improvement in the method consisted of heating boric acid over a period of 48 hr up to 250°C in a long glass tube under vacuum (3–10 mm Hg) using a sodium hydroxide–phosphorus pentoxide combination of desiccants. The product was in the form of a powder requiring but little grinding and was 99·5% pure.[13] This effect of the vacuum on the form of the product may be associated with the fact that at 10 mm Hg the dehydration of boric acid occurs in a single stage, by-passing the liquid phase which is associated with the two- or three-stage process occurring at pressures above 15 mm Hg and involving the formation of the intermediary metaboric acid, HBO_2.[14] One method of obtaining a powder suitable for use as a drying agent is to dehydrate the acid at about 800°C and to pour the melt into carbon tetrachloride at 0°C.[15] Material of exceptional fineness ($<$ 100 mμ) may be obtained by causing boron trichloride gas to react with a gaseous mixture of a hydrocarbon and oxygen with the reactants in proportions calculated to ensure completeness of the combustion.[16–17] Films of boric oxide glass can be deposited on various substrates from the vapour phase at moderate temperatures (e.g. 200°C) and low pressures.[18]

Removal of the last traces of water from boric oxide is not easy. Heating alone in air at temperatures above 1000°C does not yield a completely anhydrous product; as water is removed, water vapour from the atmosphere reacts with the melt. After establishment of equilibrium between the rates of loss and gain, the proportion of water in the melt depends on the partial pressure of the water vapour in the atmosphere.[19–21] The preparation of completely anhydrous boric oxide is claimed to be achieved by melting the sample in an induction furnace under a high vacuum. The anhydrous material has lower density than samples containing small amounts of water.[22] The presence of carbon facilitates the dehydration of boric acid at 900°C.[23] Reliable indication of the presence or absence of water in boric oxide is obtained from study of the infra-red spectra. The completely anhydrous material, such as that obtained by fusing samples in a boron trichloride atmosphere at 1350°C, does not show the characteristic and sensitive band at 2·8 μ.[24–5] Unfortunately such a fusion results, inevitably, in a fairly heavy contamination of the boric oxide with chlorine; in one experiment 2·30% was found after heating at 1300°C. A good degree of dehydration without incidental contamination can be achieved by heating boric oxide in dry nitrogen; in one instance only 0·027% of water was found after heating for 6 hr at

Table I.—Effect of Heat Treatment (under normal and reduced air pressure) on the Water Content of Boric Oxide[27]

700°C			1100°C			1200°C		
Heating time, hr	Air pressure, mm Hg	H_2O, %	Heating time, hr	Air pressure, mm Hg	H_2O, %	Heating time, hr	Air pressure, mm Hg	H_2O, %
1	760	0·27	1	760	0·20	0·3	760	0·20
2	760	0·25	2	760	0·18	2	760	0·15
4	760	0·25	4	760	0·17	4	760	0·14
			0·5	2	0·1	0·25	2	0·1
						1·75	2	0·037
			3	1	0·04	3	1	0·026
			10	1	0·023	15	1	0·020
			20	1	0·021	20	1	0·019

1300°C.[26] A recent study[27] showed that residual traces of water could not be removed entirely by heating under a vacuum, as is seen from Table I.

If, however, the heating is carried out at 1300°C under high vacuum (1 mm Hg) with the melt contained in a carbon crucible, the water content can be reduced to 10 p.p.m.[27] The density of the product decreases with decrease in the water content, in agreement with an earlier observation.[22]

Although traces of water are particularly difficult to remove from boric oxide, the rate of water absorption, and hence the value of the material as a dehydrating agent, tends to be over-estimated.[28] When in lumps, the surface of the glass acquires a milky appearance within a few hours of exposure to an atmosphere of average humidity, but thereafter the rate of absorption of more water becomes slower. The proportion of water absorbed within a specified time depends on the surface area and hence on the degree of comminution of the material. The finely divided product obtained by pouring the melt into carbon tetrachloride[15] is an efficient drying agent up to a moisture content of 25%.

In preparing boric oxide from boric acid, losses of material brought about by the volatility of boric acid cannot be avoided. Heating boric acid in an open dish may be accompanied by losses as high as 5–6%; this loss is particularly undesirable when handling expensive isotope-enriched materials. The simplest remedy is the provision of reflux conditions. In small scale laboratory preparations the volatility loss can be reduced to 1% by allowing a crust of solid to form on the surface of the dried material and by programming the heating over a period of 3–5 hr up to the maximum temperature of 500°C.[29] It is possible to achieve fairly extensive dehydration of boric acid by azeotropic distillation in organic media. In a recent process boric acid was refluxed with xylene and petroleum fractions to yield samples of product with over 95% B_2O_3 content.[30]

The preparation of isotope-enriched samples of boric oxide was attempted using zone-melting separation techniques. The heavier ^{11}B tends to accumulate in the melt but the effect is too small for the method to be of practical use.[31] Pure $^{11}B_2O_3$ can be obtained from $K^{11}BF_4$ by chemical methods; in one small scale (9·2 g $^{11}B_2O_3$) preparation an overall yield of 83% was recorded.[32]

Crystalline Boric Oxide

The existence of crystalline boric oxide was forecast in 1934[33–4] but the first successful preparation was reported in 1937.[35] The method consists in maintaining a melt of partially dehydrated boric acid (8–15% water) in a loosely covered vessel in an oven at 225–250°C. The time required varies from 7 days with the use of technical grade material to 14 days using a purer grade of boric acid. Once started, the crystallization has a tendency to proceed very rapidly and its onset can be hastened considerably by seeding. The product was claimed to be essentially anhydrous.[36–7] From a detailed study of the mechanism of the crystallization it was concluded that the separation of the crystalline HBO_2(I) from the melt is a necessary pre-requisite to the crystallization of the boric oxide itself. This conclusion is in agreement with the observations that it is impossible to obtain the crystalline product in the absence of water, even with seeding, and that heating of boric acid in open vessels yields crystals of boric oxide only if the heating is carried out very slowly. In tests under controlled conditions in closed vessels it was shown that crystallization occurs after prolonged heating below 235°C of the B_2O_3–HBO_2(I) eutectic if the water content of the melt is less than 18%. In the presence of 5% water and with addition of seed, full crystallization can be achieved within 24 hr heating at 250°C. If the water content is 1% or less the melt cannot be induced to crystallize.[38] An attempt was made to explain the difficulty of crystallizing boric oxide in terms of the mode of variation of its heat capacity in the vital temperature interval.[39]

The effects of water and temperature on the rate of crystallization were studied again in 1966; it was shown that crystallization can be induced at temperatures as low as 210°C and pressures as low as 4 kbar.[40] In 1959 the preparation of a new dense form of crystalline boric oxide from an almost anhydrous melt was reported. The method consisted of heating the oxide above 400°C and under pressures $>22{,}000$ atm.[41] It was furthermore shown that both the ordinary hexagonal form (α-B_2O_3) and the new dense monoclinic form (β-B_2O_3) can be readily prepared from boric oxide glass ($>99\%$ B_2O_3) by varying the conditions of temperature (300–600°C) and pressure (15,000–70,000 atm). Single crystals up to 0·3 mm in size were obtained. The density of the β-form, which was obtained by applying pressures $>20{,}000$ atm, was about 20% more than that of the α-form.[42–3]

MANUFACTURE

Only the vitreous form of boric oxide is manufactured on a large scale. The usual method is by dehydration of boric acid, and the simplest plant consists of a refractory-lined furnace provided with gas- or oil-fed burners, one opening for addition of solid boric acid, another opening for draining the liquid melt after dehydration and a vent or chimney for removal of gases. Various improvements or alternatives to the simple plant or process have been suggested, though not always adopted. In a patented process (1933) boric acid was fed in at the top of a carbon-lined electric-resistance heated crucible and molten boric oxide drained in a continuous stream from the bottom[44]; the energy requirement for this process was calculated.[45] More recently (1959) an apparatus for the continuous production of boric oxide based on somewhat similar principles was described in which the boric acid was passed over an electrically heated rod enclosed in a quartz tube; energy efficiencies of over 70% were claimed.[46] Quenching of the melt with water was said to be a means of facilitating fragmentation of the material[47], and the use of vacuum to obtain a lighter product was also patented.[48] The intumescence which effects

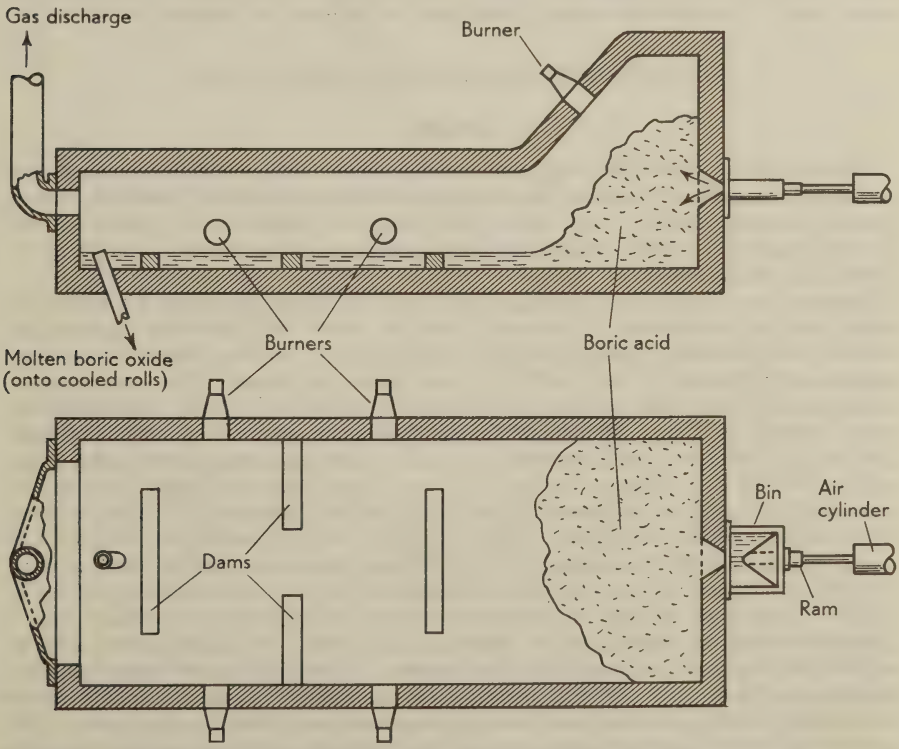

FIG. 1.—Side and top views of a furnace for the continuous production of boric oxide

considerable increase in the volume occupied by the heated boric acid can be reduced by addition of ground charcoal.[49]

A basically conventional furnace but of improved design which enables programming of the thermal treatment so as to reduce losses due to volatility of boric acid was patented in 1962 and is shown in Fig. 1. A characteristic feature of the arrangement is that the boric acid is fed continuously from inside the pile so that its temperature is raised gradually from the moment of entry into the furnace. The molten product is fed onto water-cooled rolls and immediately milled and packed in airtight containers.[50]

The relatively lower cost of borax as a source of boric oxide compared with the cost of boric acid in the U.S.A. has prompted studies of methods of preparing boric oxide from borax. One such method is based on causing borax to react with ammonium chloride in aqueous solution, precipitation and thermal decomposition of ammonium pentaborate $NH_4B_5O_8$, the intermediary compound[51–2]:

$$5Na_2B_4O_7(aq.) + 10NH_4Cl(aq.) + 13H_2O \xrightarrow[98\text{–}100^\circ]{\text{Heat}} 4NH_4B_5O_8.4H_2O + 10NaCl + 6NH_3$$

and

$$2NH_4B_5O_8.4H_2O \xrightarrow[500\text{–}900^\circ]{\text{Heat}} 5B_2O_3 + 2NH_3 + 9H_2O$$

A more direct process is based on the reaction between sodium tetraborate pentahydrate, $Na_2B_4O_7.5H_2O$, and concentrated sulphuric acid at ambient temperatures. The resulting paste-like mixture of boric acid and sodium sulphate dries to free-flowing and easily handled granules which are fed into a furnace operating at 800–900°C, similar in construction to that shown in Fig. 1, but fitted additionally with a dam on the floor to separate the boric oxide-rich ($>95\%$ B_2O_3) upper layer from the heavier layer of sodium sulphate. The product and by-product are fed onto chilled rolls from separate openings. The final product contains a small percentage of sodium oxide, but it is suitable for most applications in the glass and enamel industries.[53]

PHYSICAL PROPERTIES OF BORIC OXIDE

Density

The calculated molecular weight of boric oxide is 69·62. Determinations of the molecular weight were made on the compound in the liquid phase[54] and the gaseous phase. An average of 62 ± 9 for the formula weight of gaseous boric oxide obtained in the range 1127–1352°C shows the molecular unit to be relatively stable up to these high temperatures.[55]

Density determinations of vitreous boric oxide have been hampered by difficulties which are not adequately understood. Prior to about 1923 the data reported by various authors varied from about 1·83 to 1·85 g cm^{-3} for the material at ambient temperatures (Mellor, V, 41). In 1926 a lower figure, viz. about 1·794, was found for a sample of boric oxide prepared from pure boric acid which had been heated at about 1000°C and then quenched[56–7], but this work was subsequently criticized and a mean value of 1·844 reported for a set of samples prepared by fusing boric acid at 1400°C and annealing the product; low values were attributed to fusing the boric acid at too low a temperature and to inadequate annealing.[58–9] Alternatively, it was suggested that the figure of 1·844 was high owing to inadequate dehydration of the material heated, presumably, in a gas furnace atmosphere rich in water vapour. A product obtained by heating pure boric acid for 24 hr in an induction furnace at 1200°C under high vacuum and then allowed to cool to room temperature over a period of 13 hr was found to have density 1·812 g cm^{-3}.[22] The results of a more recent investigation confirmed that the removal of residual water brings about a decrease in the density of boric oxide; whereas a sample containing 0·28% water had density 1·853, that for nearly anhydrous material (0·002% water) was 1·829 g cm^{-3} at 20°C.[27] On the basis of density measurements made on samples with the water content down to 0·027%, a value of 1·820 g cm^{-3} for completely anhydrous material was obtained by extrapolation.[60] All the above evidence indicates that the variability in reported density values is explainable in terms of variations in the water content and in the heat treatment of the samples used in the determinations. Apart from any additional complications, similar difficulties have probably beset attempts to determine the density of molten boric oxide, so that there is some scatter of the reported data. Results obtained in four independent laboratories more recently[61–5] are shown in Fig. 2.

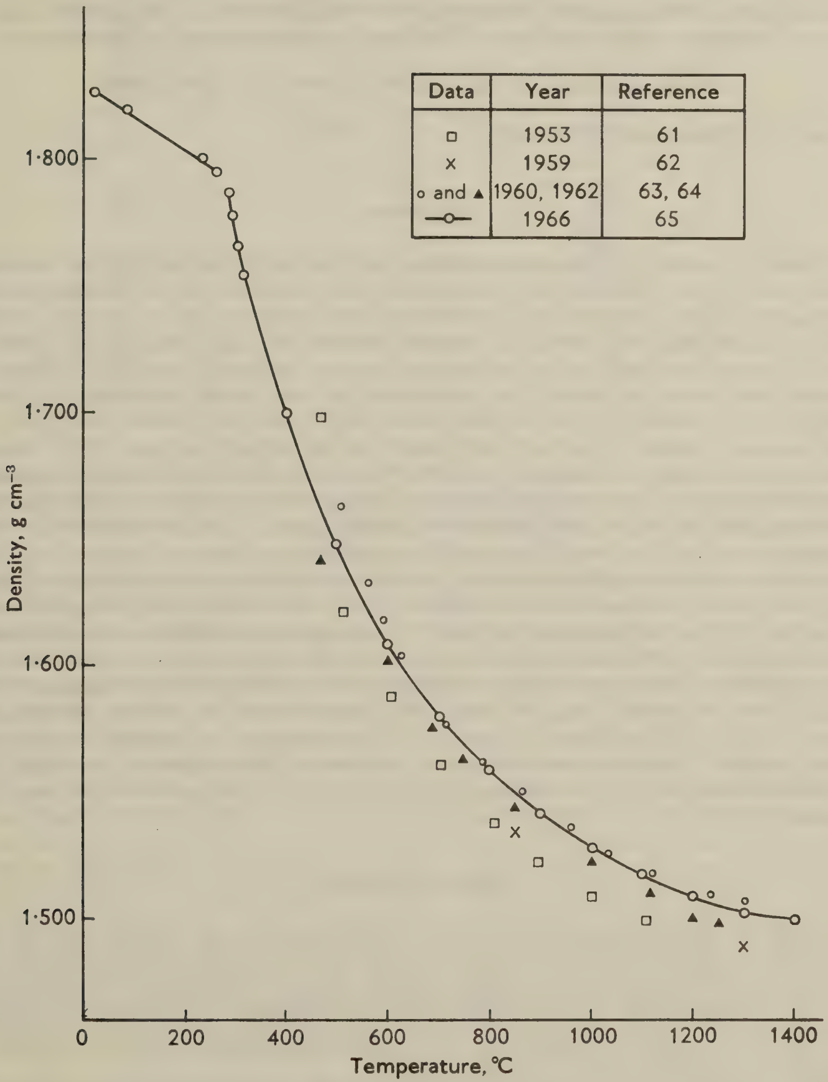

FIG. 2.—Density of boric oxide

Under one specific set of experimental conditions the density of boric oxide (in g cm^{-3}) is given by $d=K_1+K_2/T$, where T is in °K and the constants K_1 and K_2 are 1·3388 and 228 respectively over the temperature range 600–1000°C or 1·3947 and 157·9 respectively for temperatures above 1000°C.[64] According to data obtained with improved apparatus the density of boric oxide in the temperature range 1030–1310°C is given by $\rho=a-bT$(°K) g cm^{-3}, where $a=1{\cdot}633$ and $b=8{\cdot}67\times10^{-5}$.[66] In addition to the effects of moisture content and thermal history of the sample, the density of boric oxide is also affected by pressure. The degree of compaction increases gradually with the increase in pressure up to 10^4–10^5 atm.[67–9] The density of the compacted glass can be restored to the original value by annealing to sufficiently high temperatures.[67] When a pull is applied to the oxide under pressure a further increase in density takes place.[70] The compaction accompanying the crystallization of boric oxide is considerable. The density of the hexagonal or α-B_2O_3 is 2·42[35], 2·44[71] or 2·46[38,42,72], and of the monoclinic or β-B_2O_3 2·95 g cm^{-3}.[42] Pressure brings about a further compression of crystalline boric oxide and the magnitude of the effect at pressures up to 10,000 atm can be expressed by the equation:

$$-\Delta V/V_0 = (3{\cdot}24\times10^{-6})(P-2000)-(0{\cdot}29\times10^{-10})(P-2000)^2$$

where P is pressure in atmospheres.[73]

Hardness

Although frequent references are made in the literature to the hardness of vitreous boric oxide (e.g. Mellor, V, 41), there seems to be no record of any measurement having been made. The results of a scratching test carried out in a 'dry-box' in the author's laboratory on a sample of material immediately after heating it at 1300°C for 3·5 hr and quenching to the ambient temperature indicated hardness of about 4 on the Mohs scale. On raising the temperature of boric oxide the material softens gradually; the softening point as determined with a weighted needle was 250°C.[74] With another version of such a penetrometer the softening point was 209°C; above this point the 'index of plasticity' was observed to rise exponentially with temperature.[75] The 'creep', or slow deformation, of boric oxide was observed on a cylinder of the material at 243°C and under a load of 95 kg cm^{-2}. In common with other materials the deformation of boric oxide under such conditions is partly elastic in character, i.e. increasing logarithmically with time and reversing on removal of the load, and partly non-reversible, i.e. increasing at a constant rate as long as the load is applied.[76] The residual water content has an appreciable effect on the hardness of the material at temperatures below the m.p. For instance, the transformation temperature (at which the viscosity is arbitrarily 10^{13} poises) and the softening point (viscosity $=10^{7\cdot8}$ poises) are 300 and 325°C respectively for almost anhydrous (0·002% H_2O) boric oxide, but 240 and 275°C respectively for a material containing 0·28% water.[27] A rough assessment of the hardness of the hexagonal or α-form of crystalline boric oxide at the ambient temperature gave a value of 4 on the 'scale of minerals'.[35]

Thermal Expansion

Studies of thermal expansion of boric oxide glass showed that the amount of expansion per unit temperature rise increases considerably as the glass is heated above the transformation temperature and then tends to decrease as the temperature is raised above the m.p. The results of determinations of coefficients of linear and volume expansion reported by two independent authors in 1928–9 and 1933 respectively[77–9] are listed in Table II.

The transformation temperature interval between 240 and 250°C is associated with a viscosity of $10^{12\cdot7}$ poises.[78] At high temperatures the specific volume of the glass is related to its viscosity by the formula $v = K_1 + K_2/\eta$, where K_1 and K_2 are constants within a certain temperature interval. At lower temperatures there is considerable departure from linearity in the above relationship presumably owing to polymerization.[79] In a study of the pressures developed on heating samples of boric oxide contained in a steel cylinder it was shown that the then so-called 'softening temperature' rises from 248°C at 165 atm to 280°C at 3030 atm, the relationship

Table II.—Thermal Expansion of Boric Oxide Glass

Temperature, °C	Coefficient of linear expansion		Coefficient of volume expansion	
	α ($\times 10^6$) per °C	Reference	γ ($\times 10^6$) per °C	Reference
0	14·3	77, 78		
50	14·8			
100	15·2		45·5	78
150	15·7		47·0	
200	16·1		48·4	
230	16·4			
240	16·6		49·8	
250	205 (179)		615	
300	209		628	
330			629	
360			632	
500			400	79
600			270	
700			190	
800			130	
900			98	
1100			66	
1300			43	

being governed by $t_s = 247 + 0{\cdot}02p - (3 \times 10^{-6})p^2$, where p is the pressure in atmospheres. High values for t_s are obtained if the heating is too fast.[80] On closer examination of the effect of the thermal history of a sample on the variation of the coefficient of expansion with temperature, it was found that the width of transformation temperature interval increases with the duration of annealing of boric oxide. Samples quenched very rapidly from 180 to 230°C tend to contract rather than expand.[81] According to results obtained in other studies the transformation point is 247°C; below this temperature the coefficient of linear expansion is $15{\cdot}93 \times 10^{-6}$, and above it it increases rapidly. The tendency of rapidly cooled boric oxide to contract when heated below the transformation point was confirmed, but the temperature at which the contraction is at its maximum was found to be about 250°C.[82–3] The nature of changes which occur during annealing was discussed in terms of amplitudes of molecular vibrations, and their effect on the specific volume of boric oxide at 0°C was examined.[84] A review of data on thermal expansion of boric oxide reported in the literature up to about 1941 was made by Morey.[85] Data obtained more recently confirm the tendency of the coefficient of volume expansion to decrease between temperatures of 600 and 1000°C similarly to that shown in Table II[61,86] but the datum of $\gamma = 125 \times 10^{-6}$/°C at 1100°C reported by one of the authors[61] does not fit in either with the older data of Table II, or with the recent findings of a break in the thermal expansion/temperature curve at about 1000°C and a significant *decrease* in the coefficient of expansion above that temperature.[64] Residual water in boric oxide has a measurable effect on its expansion properties[60]; the coefficient of linear expansion over the temperature range from 20 to 200°C is about $15{\cdot}0 \times 10^{-6}$/°C for the almost anhydrous material (0·002% H_2O) and about $15{\cdot}8 \times 10^{-6}$/°C for boric oxide containing 0·28% water.[27]

A study of the thermal expansion of hexagonal crystalline boric oxide showed that the average value for the coefficient of linear expansion (α) increases with temperature as follows: $\alpha = 16{\cdot}0 \times 10^{-6}$/°C between 50 and 200°C, $16{\cdot}8 \times 10^{-6}$/°C between 200 and 400°C, and $70{\cdot}0 \times 10^{-6}$/°C between 400 and 450°C. Residual moisture in the sample reduces the accuracy of the results, and the presence of a small proportion of vitreous boric oxide probably accounts for a break in the expansion/temperature curve at about 200°C.[83]

Melting Point and Boiling Point

The vitreous boric oxide has no true m.p.; the transition from the solid to the liquid state takes place gradually from about 325°C, when the viscosity is $10^{7\cdot8}$ poises[27], to 450°C at which temperature the viscosity is still very high, viz. about 10^5 poises[87] and the material just begins to flow.[88] The m.p. of hexagonal (α) crystalline boric oxide was reported as between 460 and 470°C by its discoverer[35], but was quoted subsequently as 450–451°C[83] and 450 ± 2°C.[38, 89] However, some doubts on the accuracy of the latter figures persist and it was suggested in 1961 that the true m.p. is probably in the range 455–475°C.[43] The effect of residual water in boric oxide is to lower the melting, softening and freezing points of the material, viz. with 0·138% of water the m.p. (at viscosity 10^4 poises) is 543°C, the softening point (at viscosity 10^8 poises) is 346°C and the freezing point (at viscosity 10^{13} poises) is 275°C; with 0·027% water the corresponding temperatures are 551, 352 and 285°C respectively; the corresponding extrapolated values for completely anhydrous material are 552, 354 and 287°C.[26] The effect of pressure on the m.p. of α-boric oxide was estimated to produce a rise of 3°C per 100 atm.[38] The dense monoclinic form of crystalline boric oxide melts at about 510°C.[42]

The b.p. of boric oxide as calculated from vapour pressure data was reported in 1935 as 1860°C.[90] Extrapolation based on results reported by two independent teams in 1950 and 1955[91–2] gives a considerably higher figure, viz. approx. 2250°C, but lower values are obtained by calculation from vapour pressure data reported more recently, viz. approx. 2170°C[55], 2130°C[93] and 2200°C.[94]

Heat of Formation

Early attempts at determining the heat of formation of boric oxide by measuring the heat liberated on burning elemental boron in oxygen met with difficulties brought about by the impurities associated with elemental boron and by the refusal of the reaction to run to completion. The values of 349 and 336 kcal mole^{-1} (1460 and 1402 kJ mole^{-1}) reported in 1937 and 1946 respectively[5–7] were believed to be high owing to the presence of hydrogen in combination with the boron. The value obtained by burning boron in the presence of readily combustible organic material was about 281 kcal mole^{-1} (1150 kJ mole^{-1}).[2] However, a higher figure, viz. about 318 kcal mole^{-1} (1330 kJ mole^{-1}), was obtained in a calculation based on experimental data for the entropy of elemental boron[95] and the heat of hydrolysis of boron trichloride.[96] In more recent determinations carried out on crystalline boron burned using an improved method without the aid of organic material, the value of 304·6 kcal mole^{-1} (1274 kJ mole^{-1}) was obtained. This figure is in agreement with that calculated from the decomposition of diborane.[97] Data calculated from the heats of formation and hydrolysis of 99·94% pure diborane, as determined at 25°C, are as follows[98]:

$$2B(a) + 1{\cdot}5O_2(g) = B_2O_3(a) + \text{approx. } 301 \text{ kcal mole}^{-1} \ (1260 \text{ kJ mole}^{-1})$$
$$2B(a) + 1{\cdot}5O_2(g) = B_2O_3(c) + \text{approx. } 306 \text{ kcal mole}^{-1} \ (1280 \text{ kJ mole}^{-1})$$
$$2B(c) + 1{\cdot}5O_2(g) = B_2O_3(c) + \text{approx. } 305 \text{ kcal mole}^{-1} \ (1270 \text{ kJ mole}^{-1})$$

(a) = amorphous, (g) = gas and (c) = crystalline

These results are in good agreement with those of other workers[99–103] and provide reasonably close confirmation of the heat of transformation from the amorphous to the crystalline boric oxide which must be about 4–5 kcal mole^{-1} (17–21 kJ mole^{-1}).[104] The heat of formation of boric oxide is considerably higher if both reactants are in the gas phase: the calculated value is 356 kcal mole^{-1} (1490 kJ mole^{-1}) of $BO_{1\cdot5}$, i.e. 712 kcal mole^{-1} (2980 kJ mole^{-1}) of B_2O_3.[105–6] A series of diagrams representing the variation of the heat of formation of various oxides, including boric oxide, with temperature was published in 1963.[107]

Heat Capacity and Entropy

The heat capacity of boric oxide increases with temperature. The rate of increase was thought to be anomalous at about 218°C[108] and in 1931 it was reported as being above average for the boric oxide glass in the transformation range of temperatures; whereas at 100°C the specific heat was found to equal about 0·25 cal g^{-1} deg^{-1}, at 275°C it was 0·435 cal g^{-1} deg^{-1}. The shape of the specific heat/temperature curve between these two temperatures was found to be affected by the thermal history of the sample, and the paths of the curves differed according to whether the test material was being heated or cooled.[109] Ten years later the specific heat of crystalline boric oxide was shown to vary uniformly with temperature between 51 and 295°K, the values at 52·9 and 295·1°K being 1·695 and 14·72 cal $mole^{-1}$ respectively. From these data the entropy at 25°C was calculated as $S_{298 \cdot 16} = 13 \cdot 0 \pm 0 \cdot 1$ cal $mole^{-1}$ deg^{-1}.[110] Extension of the work to temperatures above ambient, on both crystalline and vitreous boric oxides, yielded a series of results that were not in agreement with the earlier conclusions about the relatively rapid increase in heat capacity with temperature in the softening range of the glass. The heat content of the crystalline boric oxide was shown to increase regularly from 298°K to 723°K according to the equation: $H_T - H_{298 \cdot 1} = 15 \cdot 75T + 7 \cdot 49 \times 10^{-3}T^2 + 5 \cdot 307 \times 10^5/T - 7139$ (cal $mole^{-1}$) and, within 1% relative error, the same relationship holds for the vitreous boric oxide up to 560°K, above which temperature there is a slight increase in the slope of the nearly linear $\Delta H/T$ curve. The heat content of the liquid boric oxide at temperatures from 900 to 1800°K is given by the equation: $H_T - H_{298 \cdot 1} = 30 \cdot 45T - 11820$ (cal $mole^{-1}$), and the heat capacity $C_p = 30 \cdot 45$ cal $mole^{-1}$ deg^{-1}. The entropy of boric oxide glass at 25°C was calculated as: $S_{298 \cdot 1} = 18 \cdot 9 \pm 0 \cdot 3$ cal $mole^{-1}$ deg^{-1}.[104] More recently (1950) a recalculation of the entropy of crystalline boric oxide based on results of measurements of heat capacity at temperatures from 17 to 200°K gave a value of $S_{298 \cdot 16} = 12 \cdot 87 \pm 0 \cdot 1$ cal $mole^{-1}$ deg^{-1}[111], i.e. close to the lower of the two values (13·0[110] and 18·9[104]) published in 1941. Close confirmation of earlier data for the heat content of boric oxide at high temperatures is also given by the equations: $H_T - H_{298 \cdot 16} = 30 \cdot 54T - 11920$ cal $mole^{-1}$ and $C_p = 30 \cdot 54$ cal $mole^{-1}$ deg^{-1}, which were computed from experimental results obtained over the temperature range 1000–2150°K.[112] The subject of the change in specific heat of glass-forming substances at the glass transformation temperature was taken up recently to show that for a mole of glass in the form of specially defined 'beads' the change was approximately $2 \cdot 7 \pm 0 \cdot 5$ cal deg^{-1} for all glass-forming materials, with the exception, it was thought, of boric oxide, for which a value of about a fifth of this was quoted.[113] It was subsequently noticed, however, that the value calculated for boric oxide was in error owing to misreading of a datum in an original paper[109] on which the calculation was based, the corrected figure being 2·75 cal deg^{-1}, i.e. well in line with that for other glasses.[114] The heat capacity and other thermodynamic functions have recently been calculated for the $^{10}B_2O_3$ and $^{11}B_2O_3$ species.[115] According to most recent (1966) data, the heat capacity of crystalline boric oxide in the temperature range 300–700°K is given by the equation: $C_p = 15 \cdot 88 + 0 \cdot 01481T - 4904T^{-2}$ cal $mole^{-1}$ deg^{-1} and the heat capacity of vitreous boric oxide in the range 300–510°K is the same. For both forms the entropy at 25°C, $S_{298 \cdot 1} = 14 \cdot 95$ cal $mole^{-1}$ deg^{-1}; this figure is a compromise between the divergent data published earlier. The heat capacity of boric oxide at its m.p. (450°C) is 31·80 cal $mole^{-1}$ deg^{-1} and the heat of melting is $5 \cdot 87 \pm 0 \cdot 03$ kcal $mole^{-1}$.[116] The heat capacity of boric oxide at low temperatures was discussed in relation to chain structure[117] and atomic coordination number[118] and a table of heat capacity data for the temperature range from 60 to 295°K has been given recently.[119]

Heat of Solution

The heat of solution of amorphous boric oxide has been reported by several authors; a short list of selected data is given in Table III.

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Table III.—Heat of Solution of Vitreous Boric Oxide

Heat of solution, kcal mole^{-2}	Year	Reference
8·0	1937	120
7·85 ± 0·08	1937	121
7·839 ± 0·020	1941	104
7·928 ± 0·029	1951	122
7·78 ± 0·05	1964	123

The above values were obtained in determinations carried out at 25°C and with proportions of added water varying from about 350 to about 1000 moles per mole of boric oxide. The heat of solution of the crystalline (α) variety of boric oxide is lower, viz. about 3·478 ± 0·020 kcal (mole B_2O_3)$^{-1}$[104] or 3·45 ± 0·03 kcal (mole B_2O_3)$^{-1}$.[123] When boric oxide is dissolved in water a considerable portion of the heat first liberated on hydration is re-absorbed during dissolution of the boric acid formed; i.e. the heat of hydration of one mole of boric oxide to two moles of boric acid, H_3BO_3, is considerably higher than the heat of solution, viz. 18·6 kcal per mole of vitreous B_2O_3 at 239°K[120] or quoted as 18·26 ± 0·08 kcal per mole of vitreous B_2O_3.[122] In a study of hydrothermites (heat-releasing mixtures) boric oxide evolved approx. 16·8 kcal mole^{-1} on hydration.[124] The heat of neutralization of vitreous boric oxide with 0·1N sodium hydroxide is 24·7 kcal mole^{-1}.[121]

Vapour Pressure

All aspects of the volatility of boric oxide are of considerable practical interest, particularly in the various branches of the glass industry where its use is indispensable. Much effort has been rewarded with rather scant and relatively low-precision data for reasons which will become apparent from the following account of the last few decades' studies. The volatility of boric oxide was observed over a century ago[125] and confirmed since[126–7]; nevertheless as late as 1922 an attempt to measure the vapour pressure at about 1540°C was not successful.[128] The first results of a quantitative study, reported in 1935, are given in Table IV.

Table IV.—Vapour Pressure of Boric Oxide[90]

Dynamic Method, 1935

Temperature, °C	$p_{B_2O_3}$, mm Hg
1200	0·83
1250	2·0
1300	3·4
1350	6·9
1400	12·0

The determination was carried out by the dynamic method using nitrogen gas under normal atmospheric pressure[90]; the results were in later years criticized as being much too high. In 1937 a few data were reported in terms of weight loss, viz. 0·0861 g and 0·1470 g of boric oxide lost per cm^2 of evaporating area per 24 hr at 1250 and 1350°C respectively[129]; the ratio of the two weight losses given is not in good agreement with the ratio of the vapour pressures at the corresponding temperatures quoted in Table IV. Assessments of boric oxide losses from glass and ceramic compositions yielded widely different results; whereas no significant losses were observed from boric oxide alone or mixed with other anhydrous constituents of glass batches at temperatures up to 1400°C[130], the volatilization of boric oxide on heating glaze compositions was reported to commence at 450°C.[131] The results of studies of volatility of boric acid carried out in 1937[120], and particularly the finding that as much as 5·6% boric acid can be lost on dehydrating it at 500°C[130], might have warned later workers. Nevertheless, for another 25 years or so, the far-reaching effect of water vapour on the volatility of boric oxide was not fully appreciated. In 1950 an improved technique based on measuring the rate of effusion of vapour from an orifice in a platinum Knudsen cell was applied to the determination of the vapour pressure of boric oxide at temperatures from about 1300 to 1650°K; a few of the results are quoted in Table V.

Table V.—Vapour Pressure of Boric Oxide[91]

Effusion Method, 1950

Temperature		Pressure	
°K	°C	$P_{B_2O_3}$, atm	$p_{B_2O_3}$, mm Hg
1449	1176	$9·499 \times 10^{-6}$	0·007
1540	1267	$6·526 \times 10^{-5}$	0·050
1569	1296	$6·900 \times 10^{-5}$	0·052
1631	1358	$2·310 \times 10^{-4}$	0·176
1642	1369	$3·050 \times 10^{-4}$	0·232

On the basis of the data quoted in Table V the dependence of vapour pressure on temperature can be expressed by the equation $\log P_{(atm)} = 6·742 - 16{,}960/T$, where T is in °K.[91] The above results were confirmed and in 1955 the same equation was found to be valid over an extended temperature range, viz. 1331–1808°K[92]; more confirmatory evidence was published in 1957.[132] Similar results for the temperature range 1000–1300°C were also obtained using an improved effusion method whereby the condensate is weighed on a microbalance[133], and a very similar equation, viz. $\log P_{(atm)} = 6·56 - 16{,}805/T$ was proposed in 1960.[134] However in 1957 a set of significantly lower vapour pressure values was published. The determinations were carried out by measuring (entirely under vacuum) the weight and force exerted by the boric oxide vapour effusing through two small circular orifices and the results fitted the equation: $\log P_{(atm)} = 7·771 - 19{,}010/T$.[55] A selection from still lower values obtained in 1963 is given in Table VI.

Table VI.—Vapour Pressure of Boric Oxide[135]

Effusion Method, 1963

Temperature		Pressure	
°K	°C	$P_{B_2O_3}$, atm	$p_{B_2O_3}$, mm Hg
1436	1163	$4·98 \times 10^{-6}$	0·004
1462	1189	$9·94 \times 10^{-6}$	0·008
1486	1213	$1·66 \times 10^{-5}$	0·013
1496	1223	$1·99 \times 10^{-5}$	0·015
1509	1236	$2·65 \times 10^{-5}$	0·020
1532	1259	$4·23 \times 10^{-5}$	0·032
1543	1270	$5·14 \times 10^{-5}$	0·039

The above data fit the equation $\log P_{(atm)} = 8·921 - 20{,}381/T$. It was suggested that the values obtained in all earlier determinations made with the use of the Knudsen cell (i.e. including those given in Table V) were high owing to exposure of the test samples to water vapour from the atmosphere.[135] This conclusion is strongly supported by observations made in recent years on the profound effect of water vapour on the volatility of boric oxide[93, 136–8], the difficulty of obtaining truly anhydrous starting material[27] and the readiness with which water vapour reacts with molten boric oxide.[21] A review of measurements of the vapour pressure of boric oxide made up to about 1960 is available[139], and a brief critical assessment of data up to 1963 has been made by the authors of the data given in Table VI.[135] Controversy on this subject, however, continues. In a paper published in 1964 it is claimed that the considerably higher data obtainable by the inert gas-flow method (Table IV) are more accurate.[140] In 1966 results of an examination of vapour pressures at higher temperatures were reported.[94] The material used was freed from water and oxygen contaminants (the latter interfere by giving rise to formation of BO_2[141]) by degassing at 1200°C with purified argon. A selection of results by direct boiling point and transpiration vapour measurements is given in Table VII:

Table VII.—Vapour Pressure of Boric Oxide[94]

Boiling Point and Transpiration Methods, 1966

Temperature		Pressure	
°K	°C	$P_{B_2O_3}$, atm	$p_{B_2O_3}$, mm Hg
Boiling point method			
1946	1673	$1{\cdot}48 \times 10^{-2}$	11·3
2083	1810	$5{\cdot}62 \times 10^{-2}$	42·7
2273	2000	$2{\cdot}46 \times 10^{-1}$	187
2419	2146	$7{\cdot}94 \times 10^{-1}$	603
Transpiration method			
1956	1683	$1{\cdot}47 \times 10^{-2}$	11·2
2087	1814	$5{\cdot}11 \times 10^{-2}$	38·8
2094	1821	$4{\cdot}77 \times 10^{-2}$	36·2

The above data fit the equation: $\log P = (7{\cdot}124 \pm 0{\cdot}064) - (1{\cdot}763 \pm 0{\cdot}055) \times 10^4/T$ and, if extrapolated to lower temperatures, would support the data obtained by the effusion method in 1963 (Table VI). The mechanics of evaporation and their likely effect on the results obtained by effusion have been studied[133, 142] and the 'condensation coefficient' for boric oxide was found to be close to unity.[143] The results of a study of the composition of the vapour phase above boric oxide at temperatures up to 2400°K showed the volatile species to consist largely of B_2O_3(g) with less than 5% of B_2O_2(g), BO(g) or either of the two elements in the gaseous form.[144–5] The dissociation at temperatures up to 1515°K was found to be less than 3%.[134] The thermodynamics of the evaporation were studied by mass spectrometric methods[146–7], and B^+, BO^+, $B_2O_2^+$ and $B_2O_3^+$ ions were found to be present in B_2O_3 vapour at the relative intensities of 2, 7, 7 and 100 respectively.[147] Importance of knowledge of vapour pressure data for boric oxide has been emphasized in connection with a study of the performance of pentaborane-containing fuels.[148] A practical use of the volatility of boric oxide with water vapour has been suggested in proposed processes for the recovery of boric oxide from borate minerals.[149, 150]

Heat of Vaporization and Sublimation

Just as with improvement in the experimental technique successive determinations of the vapour pressure of boric oxide yielded smaller and smaller values, so the calculated values for the heat of vaporization of boric oxide have been found to be higher with each successive attempt. A summary of reported data is given in Table VIII.

Table VIII.—Heat of Vaporization of Boric Oxide

Heat of vaporization, kcal (mole B_2O_3)$^{-1}$	Year	Reference
65·6	1935	90
77·6	1950	91
89·4 (ΔH_0°)	1955	92
87 (ΔH_{1500})	1957	55
89·32 (ΔH_0°)	1960	134
84·5 (ΔH_{1500})	1962	147
93·3 (ΔH_{1500})	1963	135
93·6 (ΔH_{1800})	1963	151

The heat of sublimation of boric oxide was reported in 1957 as 88·7 kcal mole^{-1} at 0°K[132], but in 1963 the value was found to be 103·1 ± 0·1 kcal mole^{-1} at 25°C (298°K).[135] The thermodynamic properties of the molecules of boric oxide vapour have been studied (1964) after trapping them in a solid inert gas at 4 or 20°K.[152]

Viscosity

In common with other 'glass former' oxides, molten boric oxide has a high viscosity. Some of the earliest data obtained by the torsion balance method showed the viscosity to decrease from 1510 poises at 650°C to 542 poises at 750°C.[153] Results published in 1935[154] and given in Table IX are typical and not widely different from more recent data.

Table IX.—Viscosity of Boric Oxide[154]

Temperature, °C	Viscosity (η), poises	Temperature, °C	Viscosity (η), poises
260	$6{\cdot}1 \times 10^{11}$	600	$4{\cdot}8 \times 10^3$
300	$4{\cdot}4 \times 10^9$	700	$8{\cdot}5 \times 10^2$
360	$2{\cdot}0 \times 10^7$	800	$2{\cdot}6 \times 10^2$
400	$1{\cdot}6 \times 10^6$	900	$1{\cdot}2 \times 10^2$
450	$1{\cdot}7 \times 10^5$	1000	$7{\cdot}4 \times 10$
500	$3{\cdot}9 \times 10^4$	1100	$4{\cdot}3 \times 10$

A set of results obtained independently in 1942[155] is in good agreement with the data given in Table IX. In 1937 the equation $\log(\eta/2{\cdot}114) = 1450/(t - 150{\cdot}8)$ was proposed as representing the dependence of viscosity on temperature up to 1100°C.[156] This was followed by attempts to evolve a generalized theory, and equations in the form $\log \eta = A + B/T$ (where η = viscosity in poises, and A and B are constants) were proposed.[157–8] The plot of $\log \eta$ versus $1/T$, however, does not give a straight line and further attempts were concerned with modifications of the simple equation which would fit more accurately the available data.[159] A straight line was obtained by plotting $(1{\cdot}5 \log T - \log \eta)$ versus $1/T$, so that an equation of the form: $\log \eta = A + B/T + 1{\cdot}5 \log T$ was claimed to fit a number of inorganic liquids including boric oxide.[160] Pressure has a considerable effect on the viscosity of boric oxide; in a study using a capillary-flow method it was shown that the effect of raising the pressure from 1 atm to 1000 kg cm^{-2} was to raise the viscosity 4·48 times at 359°C and 1·58 times at 516°C.[161] Boric oxide can be used for calibrating viscometers[162], but since the material is hygroscopic it must be dehydrated before use; mere heating for 2 hr at 1300°C, as recommended in one instance[163], may not be adequate, but the water content can be reduced to 0·027% by heating for 6 hr at 1300°C in dry nitrogen.[26] Viscosity determinations have been made more recently by several independent workers over the following ranges of temperature; 500–1280°C[162], 450–1200°C[87], 500–800°C[164], 500–1000°C[86], 850–1300°C[62], 500–1300°C[165], 115–1270°C[163,166], 318–1400°C[167] and 370–1280°C.[168,169] Agreement among the various data (including those quoted in Table IX) is fair, the differences being ascribable to variations in the purity of the test material and the experimental technique.[165] A set of results obtained very recently with an improved counterbalanced-sphere viscometer fits the equation: $\log \eta = -0{\cdot}6672 + 3472/T$(°K) over the temperature range 1000–1400°C, where η is viscosity in poises.[66] The effect of retained water is to lower the observed viscosity.[26,62,163] On extrapolating results obtained on a series of samples with water contents varying between 0·49 and 0·027% to water content nil, the following equation was proposed for the anhydrous material: $\log \eta = 0{\cdot}652 + 1215/(t-189)$ with t in °C. A review of data reported between 1907 and 1956 indicates that all these data fall between the values expected for boric oxide with water content varying from nil to about 0·4%.[26,170]

The 'activation energy for viscous flow', which for non-associated liquids is defined by the Arrhenius equation: $E_\eta = RT \log \eta/A$ (where η is viscosity in poises and A is a constant) was determined for boric oxide in 1956; the value of approx. 34 kcal mole^{-1} was found over the temperature range 500–800°C.[164] Subsequently values have been quoted varying from the maximum of 100 kcal mole^{-1} in the transformation range ($\eta = 10^{11}$ poises)[166] to 36·5 kcal mole^{-1} at 520°C, or 12·5 kcal mole^{-1} at 1000°C[86], or 15 kcal mole^{-1} at 1300°C[62], or about 12 kcal mole^{-1} at 1300°C. The overall conclusion was that the 'activation energy for viscous flow'—temperature relationship for boric oxide is complex and cannot be described by the Arrhenius equation or even by any equation of the form $E_\eta = A/T + B$ which is applicable to the majority of associated liquids.[171] Two other equations of this form, however, have been subsequently proposed, viz. $E_\eta = 4{\cdot}213 \times 10^4/T - 22{\cdot}15$ for the temperature range 500–775°C and $E_\eta = 1{\cdot}121 \times 10^4/T + 7{\cdot}40$ for temperatures above 775°C.[165] The effect of water in boric oxide is to lower the activation energy for viscous flow at high viscosities (e.g. from 160 to 105 kcal mole^{-1} at 10^{13} poises) and to raise it at lower viscosities (e.g. from 32·6 to 33·8 kcal mole^{-1} at $10^{4\cdot5}$ poises and from 13·9 to 17·1 kcal mole^{-1} at 10^2 poises).[26] A series of recent studies has been concerned with the examination of relationships between ultrasonic absorption or velocity and the viscosity of vitreous and liquid boric oxide.[172–5]

Surface Tension

The surface tension of boric oxide was reported in 1938 to vary from approx. 57 dynes cm^{-1} at 300°C to approx. 67 dynes cm^{-1} at 500°C; these values were determined by the sessile drop method.[176] In 1947 a study made using a modification of the pull-on cylinder (or 'anchor ring') method yielded a set of results fitting the straight line equation: $\gamma = 47{\cdot}6 + 0{\cdot}0354t$ (γ is in dynes cm^{-1} and t in °C) over the temperature range at least 700–1400°C.[177] Results quoted in succeeding years were, on the whole, in good agreement with those given by the above equation[178–80]; a typical set obtained using the maximum bubble pressure method is given in Table X.

Table X.—Surface Tension of Molten Boric Oxide[181]

Temperature, °C	Surface tension, dynes cm^{-1}
866	79·4
1000	82·3
1100	86·1
1229	94·4
1331	103·4

Molten boric oxide is one of the few oxides the surface tension of which increases with temperature (others being GeO_2 and SiO_2, but not Al_2O_3 or P_2O_5) and, not surprisingly, attempts have been made at explaining this unorthodox behaviour. According to one plausible theory the spatial asymmetry of the boric oxide molecule results in a strong tendency to orientation in the surface layer so as to give the lowest possible surface tension. On raising the temperature, the disorder brought about by the increasing thermal agitation of the molecules reduces the degree of orientation in the surface layer and so leads directly to an increase in the surface tension.[182] It is also conceivable that as a further result of this thermal agitation, other molecular species with higher surface tension are brought to the surface from the bulk of the melt.[183] In amplification of the second concept it is suggested that the degree of association of the molecular species brought from the bulk of the liquid to the surface decreases with temperature thus accounting for, or at least contributing to, the increase in the surface tension.[179] Although a strict mathematical treatment of the separate contributions of these various factors to the observed increase in surface tension with temperature is not possible[179], there is no conflict between the postulated mechanisms, and it appears safe to conclude that all the factors mentioned above are operative.

Refractive Index

The refractive index of a sample of quenched boric oxide glass was reported in 1935 as $n_D = 1{\cdot}4577$[184], and in the following year as $n_D = 1{\cdot}458$.[185] However, results of determinations carried out at about the same time on a large number of samples were found to vary from 1·4502 to 1·4633, according to the treatment (particularly the thermal history) of the samples; the 'best' value obtained on a sample heated for 48 hr in a vacuum and allowed to cool to 25°C over a period of 13 hr was thought to be $n_D = 1{\cdot}4582$, the accompanying values for the specific refraction being $r = 0{\cdot}1506$ and for the molecular refraction, $R = 10{\cdot}49$.[22] Since about 1960 considerable interest has been shown in the effects of the water content and thermal history on the optical and other properties of vitreous boric oxide, and a number of observations have been published.[27, 60, 186] Typically, whereas the refractive index of a sample containing 0·28% water is $1{\cdot}4655 \pm 0{\cdot}0005$, a practically 'waterless' sample (20 p.p.m. H_2O) was shown to have $n_D = 1{\cdot}4585 \pm 0{\cdot}0003$.[27] The effect of temperature is to decrease the value of the index[187], and the effect of pressure is to increase it, as might be expected.[68] The refractive indices of the hexagonal or α-B_2O_3 are $n_\alpha = 1{\cdot}615$ and $n_\gamma = 1{\cdot}648$, and for the dense, β-variety of crystalline boric oxide the corresponding indices are 1·693 and 1·701 respectively.[41]

Boric oxide is a component of many fluorescent, phosphorescent and luminescent systems (Mellor, V, 42). A phosphorescent glass is obtained when boric acid is ignited at 800°C with a mere trace of saccharose.[188] Some earlier attempts to elucidate the mechanism of the action of boric oxide in such systems[188–9] have not been followed up, the papers published being largely confined to practical details of preparation and to descriptions of the properties of the various products. These contain, in addition to boric oxide, typically: zinc, cadmium or beryllium phosphates[190]; zinc and cadmium oxides[191]; calcium or magnesium tungstates[192]; zinc oxide with manganese activator[193], barium, strontium and magnesium phosphates[194] and magnesium oxide and fluoride with titanium ammonium fluoride activator.[195] It is now accepted that the main function of boric oxide, like that of other rigid solvents, is to reduce the number of collisions between the molecules in the phosphorescent state and thereby to reduce the dissipation of energy to routes other than via the long-life or β-phosphorescence.[196]

Electrical Conductivity

The electrical conductivity of boric oxide is very low. At 300°C, for instance, it is 5×10^{-14} mho cm^{-1}.[197] On raising the temperature, and as the viscosity decreases, there is a gradual increase in conductivity without discontinuities on transition from the glassy to the liquid state.[109] In the temperature range 600–1200°C straight, or nearly straight, lines are obtained on plotting the logarithm of specific conductivity versus the reciprocal of temperature.[198, 87] The dependence of conductivity on temperature is given by the general equation: $\log \kappa = A - B/T$, where κ = conductivity in mhos cm^{-1} and A and B are constants.[86, 199] Alternatively, $\kappa = A_\kappa \exp\{-E_\kappa/RT\}$, where E_κ = activation energy for conduction which equals 27[86] or 26 kcal mole^{-1}.[62] The last value is supported by a set of recent results which show that E_κ remains constant even when the conductivity values are affected appreciably by the degree of purity of the sample used.[200] Assuming that the purer the sample, the lower the conductivity, the 'best' approximate equation relating conductivity and temperature is probably: $\log \kappa = 0{\cdot}3 - 5900/T$.[137] However, the effect of residual water content on the conductivity of boric oxide has not yet been examined, so that for a completely water-free material the conductivity may be less than that given by the above equation.

Dielectric Constant

The dielectric constant of boric oxide at ambient temperatures and at low frequencies is about 3·5.[109] It is hardly affected by the temperature until the oxide is heated above 400°C when a steep rise occurs. A few typical results illustrating the dependence of this constant on the temperature are listed in Table XI.

Table XI.—Dielectric Constant of Boric Oxide[164]

Temperature, °C	Dielectric constant		
	10^3 cycles s^{-1}	10^4 cycles s^{-1}	10^5 cycles s^{-1}
25	4·15	—	3·18
240	3·42	—	3·16
355	3·66	—	3·19
410	5·54	—	3·28
445	20·0	—	3·45
570	—	26·3	—

The above data show that the dipole moment of boric oxide is about 3·5 debyes.[164] The dielectric loss (tan δ) of vitreous boric oxide is small ($<0{\cdot}1$) and, like the dielectric constant, fairly independent of temperature up to about 400°C at frequencies of the order of 10^5–10^7 cycles s^{-1}[164, 201]; at 50 cycles s^{-1} there is a significant increase in the value with temperature, viz. from 3×10^{-4} at 200° to 4×10^{-2} at 350°C.[197, 202] Dielectric constant and dissipation data at low frequencies (1–50 kc s^{-1}) and temperatures of 500–800°C have been published.[203]

STRUCTURE OF BORIC OXIDE

Vitreous Boric Oxide

Boric oxide of all oxides is the one in which the oxygen is bound most firmly[106], and it displays the strongest tendency to form a glass.[204] The structure of the vitreous form of this compound has, therefore, been of immense interest to physicists, chemists and glass technologists.

Like other glasses vitreous boric oxide is a supercooled liquid which shows little tendency to crystallize. When heated it softens to form a viscous liquid without showing a definite m.p. Fracture of the solid does not take place along a plane but along a curved surface and a characteristic conchoidal surface results. *X*-Ray examination shows that the atoms are linked by the same type of bond as in a crystal, the essential difference being that there is no order or symmetry in the arrangement of the groups or units present.[204] The idea of a 'unit', i.e. strict order within a very small group of atoms, it will be noted, is indispensable. In a boric oxide glass the BO_3, or more precisely $BO_{1\cdot5}$, units are planar and linked to each other so as to form an irregular network as shown in Fig. 3. Evidence collected over the years supports some facets of the random network theory. In particular it was confirmed, on the basis of Fourier analysis data of *X*-ray patterns, that the boron atoms are 3-coordinated, i.e. the units are planar, the distance between each boron and oxygen atom being 1·39 Å and between two oxygen atoms 2·40 Å.[205–6] A more recent (1958) *X*-ray study yielded confirmation of triangular coordination, the interatomic distances being given as 1·37 and 2·37 Å respectively.[207] Further confirmation of the planar arrangement of atoms within the $BO_{1\cdot5}$ unit comes from nuclear magnetic resonance studies[208–9] and from infra-red absorption spectra.[210]

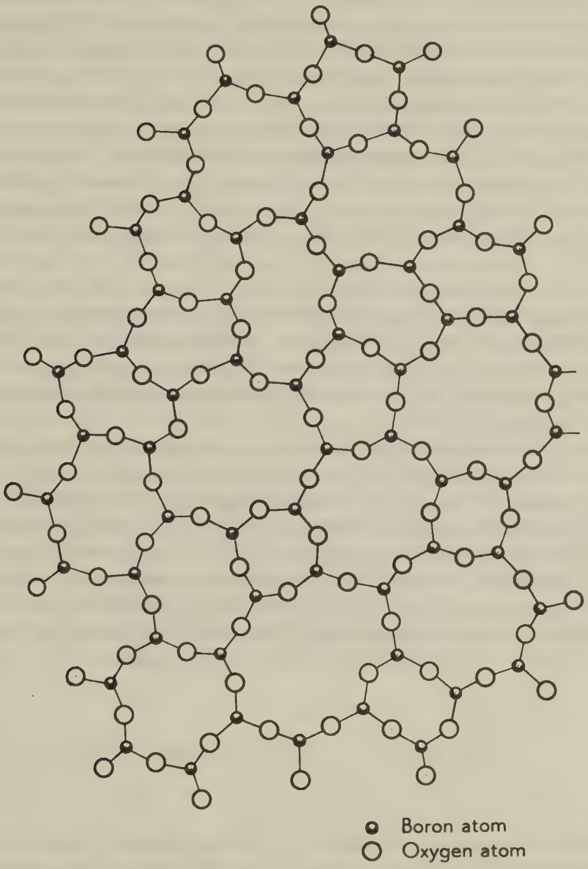


FIG. 3.—Simplified pictorial presentation (two-dimensional analogy of a three-dimensional arrangement) of the glass structure of A_2O_3-type oxides

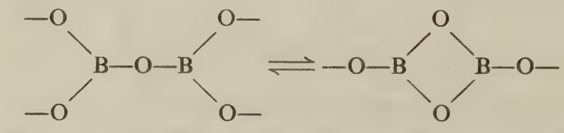
Courtesy of the Journal of the American Chemical Society

Publication of the simple network theory was followed in 1935 by a contradictory observation. In the Raman spectrum of vitreous boric oxide an intense line at 810 cm^{1-} and weak lines at 1120 and 1257 cm^{-1} were found.[211] This observation was confirmed by another worker who gave a mean frequency difference of 806 cm^{-1} for the strong Raman line and concluded that there must be a more structural order in boric oxide glass than had previously been suspected.[212] The Raman line was observed subsequently by several workers and the 'best' figure for the frequency difference was found to be between the above two, i.e. 808 cm^{-1}.[213–14]

In 1952 it was suggested that neither the two-dimensional layer structure nor a three-dimensional network structure is compatible with some of the properties of boric oxide, and it was proposed that the vitreous form of the oxide at temperatures below 300°C is made up of B_4O_6 units held together by weak forces of the van der Waals type. This structural unit was suggested to consist of a cage in the form of a tetrahedron with boron atoms at the corners and one oxygen atom between two boron atoms. Such a structure would be compatible with the relatively low m.p. of boric oxide and the considerable decrease in its coefficient of volumetric expansion at temperatures above 500°C when the structure would change into a 'stronger', i.e. coordinative type.[215] The basic concept of the existence of such a structural unit was supported by data derived from infra-red and Raman spectra.[216–22] Some authors extended the original claim to proposing that the cage molecule preserves its structure when the solid is heated above the softening point up to a temperature of 1000°C.[220]

In 1953 a layer graphite-like structure was claimed having BO_3 as the unit group[223], but this idea was soon followed first by interatomic data which seemed to support the presence of BO_3 tetrahedra as the fundamental units[224], and thereby the view that both single and double layers of BO_3 groups are present.[225] Some of the conclusions, especially with reference to the reported B–B distance of 1·85 Å, were shown to be invalid.[226–7]

Objections to the concept of B_4O_6 cage molecules were raised, originally mainly on the basis of viscosity data. The essence of the argument was that the energy of activation for viscous flow, i.e. 36·5 kcal (mole B_2O_3)$^{-1}$ at 520°C, was too high to correspond to the breaking of the weak bonds of van der Waals type which were presumed to hold the B_4O_6 molecules together.[86, 227–8] On the other hand, the relatively low enthalpy of fusion of boric oxide forbids the assumption of the breaking of boron–oxygen bonds on a large scale.[164] It was proposed that the structural units compatible with the available viscosity data and with the B–O bond strength of about 100 kcal mole^{-1} in liquid boric oxide are as shown:

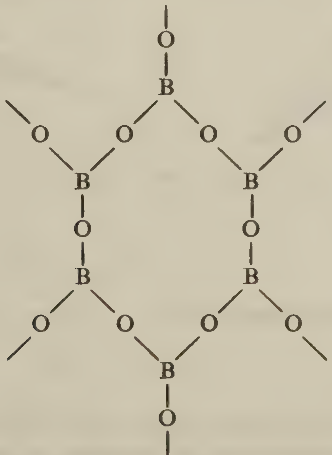


This equilibrium is of course affected by the temperature, and the energy change involved in the above rearrangement would be of the order found for the energy of activation for viscous flow.[229] As the temperature is raised the appearance of polar —B=O groups is possible by rearrangements which need not involve ionic dissociation[62]; the rapid increase in the dielectric constant on raising the temperature above about 400–500°C[164] is presumably a direct result of the appearance of the —B=O group. In defence of the B_4O_6 molecule unit it has been pointed out that four dative B → O bonds per cage molecule at 520°C and two such bonds at 1000°C would be in agreement with the energy of activation for viscous flow[230], but no final proof for the existence of the cage molecule structure is available.

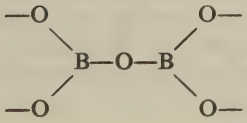
A few alternative proposals for the structure of boric oxide have been made, some of which can be rejected in the light of subsequent evidence but others appear to offer interesting possibilities. The suggestion that the glass consists of $B_9O_{14}^-$ units held together by hydrogen bonds, with one out of each nine boron atoms tetrahedrally coordinated[231], can be dismissed on the ground that boric oxide can be dehydrated to the extent that there would not be enough hydrogen retained to allow the suggested size of a unit; also, since bonding of hydrogen to the ⟩B—O— group is considerably stronger than in water, formation of hydrogen bridges in the presence of BO_3 groups is unlikely.[232] The possible presence in vitreous boric oxide of the tetrahedrally coordinated boron atom has also been extensively discussed.[233-9] Its presence would be in agreement with the low viscosity of boric oxide at high temperatures and its marked degree of compressibility. It was also suggested that a change from 3 to 4 coordination number might be induced by external forces, e.g. pressure. However, extensive evidence now accumulated all points to the virtual absence of tetrahedral coordination in vitreous boric oxide. Results to this effect have been obtained in examinations of infra-red spectra[210] and in nuclear magnetic resonance studies[208, 240-3] in some of which it was also shown that there is no change in the coordination number on application of high pressures.[241-2]

Investigations into the structure of vitreous boric oxide have been rendered difficult by the presence of residual water. In some infra-red studies[231, 234, 244] the results were thus affected, so that the conclusions drawn, e.g. concerning similarities between the vitreous and crystalline forms of boric oxide, were not always correct.[245-8]

Discussions of controversial opinions published in the technical literature have made a valuable contribution to the problem of the structure of boric oxide without, however, yielding a generally acceptable theory. However, if the remaining ideas and suggestions made on this subject are reviewed in chronological order, although they are mostly unrelated to each other, they appear to lead naturally to a theory which is in agreement with the facts known to date. In 1937, on the basis of an assumption that boric oxide melt is an associated liquid, the association number of B_2O_3 units was calculated to be 60 at 450°C and 18 at 1100°C from a formula involving specific heat, density and viscosity data.[54] In 1953, on the basis of similarity in the Raman spectra, viz. the strong line at 808 cm^{-1}, it was suggested that boric oxide has a boroxole ring structure.[213] In 1955 the mechanical and electrical relaxation processes of boric oxide as an 'amorphous polymer' were studied along lines similar to those used for typical organic polymers.[249] Chain structures were proposed from 1954 onwards[250-3] and positive evidence of elastic properties of boric oxide similar to those of typical polymers was reported in 1960.[254-5] In 1961 it was shown that the intensity of the Raman 808 cm^{-1} line decreased rapidly as the temperature was raised from 450 to 800°C.[256] A suggestion that boric oxide is an associated molecular liquid with a relatively large flow unit was again made in 1963.[257] A model of the form:



was suggested as fitting the Raman and infra-red data (with some reservations), and



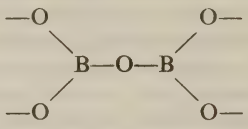
was proposed as the repeating unit in 1963.[258] The basis on which the above assumptions were made was questioned.[259] Nevertheless the original idea has been further developed by suggesting that the units combine in one plane to give a layered structure and are held together by dative bonds.[65]

A few of the indisputable, or at least fairly generally acceptable, facts listed as follows are of special significance[260]:

(i) A planar triangular $BO_{1\cdot 5}$ group is the basic unit of boric oxide structure.

(ii) The Raman spectra of boric oxide and boroxole ring are similar.

(iii) The assumption of the presence of the



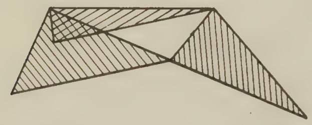
group (though not necessarily as a basic unit) is very plausible.

(iv) There are strong indications of a polymeric chain structure, the chains being fairly long at the m.p. but decreasing in length with rise in the temperature.

(v) The value of the dielectric constant increases rapidly as the temperature is raised above the m.p.

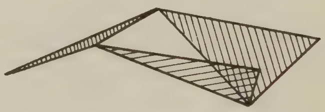
(vi) The intensity of the Raman 808 cm^{-1} line decreases rapidly with increasing temperature above the m.p.

In connection with point (ii) above it should be noted that the boroxole ring need not be strictly in one plane for condition (i) to apply. The structure could be:

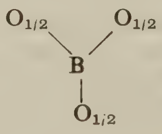


I

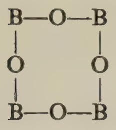
or



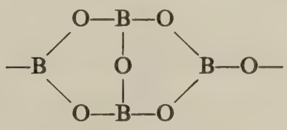
II

where each shaded triangle represents one  group.

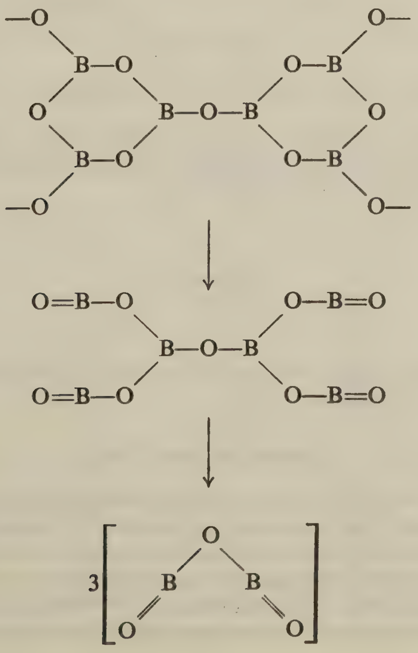
Assuming a puckered ring structure to be possible, version (**II**) appears to be the more likely, and it can be shown that it is capable of giving rise to formation of chains through random joining of two neighbouring rings via, alternatively, two and one of the available three oxygen corners; occasional bonding of one ring to three other rings would give rise to branching of the chains. It is of interest to note that the joining of two model **II** rings through two oxygen atoms gives rise to a unit element of cubic symmetry because four boron atoms then lie in one plane; on compression and flattening of the rings the oxygen atoms would also be brought into the same plane to give the



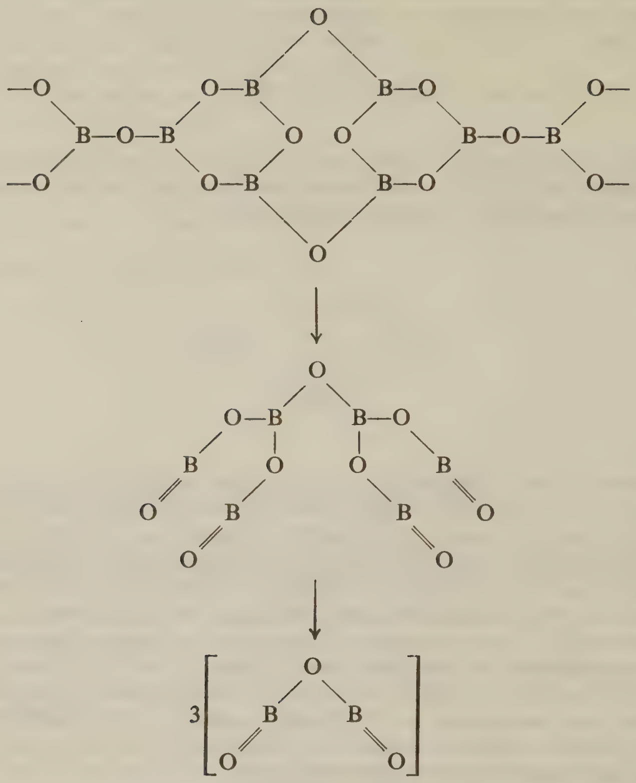
unit found in crystalline boric oxide (*vide infra*). It is conceivable that in addition to the boroxole ring, the $BO_{1\cdot5}$ unit as such may take part in the formation of chain structures by joining onto a boroxole ring to give



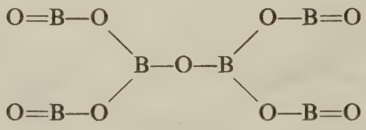
The presence of what appears to be the less likely structural form of the boroxole ring, viz. according to model **I** above, would give rise to a B_6O_9 cage made of a pair of boroxole rings. If, however, the structure is based on model **II** of the boroxole ring (which would lend itself to building up into open chains, branched chains and closed chain structures) it is easy to visualize the rupture of B—O bonds in any proportion of the whole, including that which satisfies the observed value of about 36 kcal (mole B_2O_3)$^{-1}$ as the energy of activation for viscous flow at about 500°C. It must be remembered that only the actual rupture of the B—O bonds (and not the breaking of B → O dative bond) can result in the formation of the polar —B=O groups which are responsible for the rapid increase in the dielectric constant at, and above, the m.p. The last stages in the break-up of the boroxole ring network at high temperatures would be represented by:



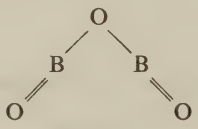
or by:



The break-up of the network into



units is probably far advanced at about 1400°C, above which temperature the structure tightens and a marked decrease in the expansion coefficient of the liquid is noted.[261] The final break-up into the



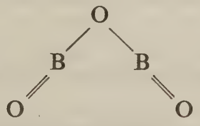
units is greatly facilitated by water, which explains the profound effect of water on the rate of volatilization of boric oxide.

Crystalline Boric Oxide

Largely owing to the difficulties associated with the preparation of crystalline varieties of boric oxide, their structure has received less attention. A possible structural relationship between them and metaboric acid was hinted at in 1944[262], but it was not until 1952–3 that the results of examination of the *X*-ray powder patterns of the α or hexagonal crystals were published.[71, 263–4] The conclusions were that the unit cell is hexagonal and that the structure consists of two types of BO_4 tetrahedra with three of the corners shared by two tetrahedra[71, 263] to yield a form of BO_4 spiral.[264] Doubts were expressed[265] concerning the validity of these conclusions which, in fact, are not in accord with more recent findings on the absence of tetrahedrally coordinated boron in densified boric oxide. However, two observations made in the above study, viz. (a) the measured density of 2·44 indicates the presence of $3B_2O_3$ groups per unit cell[71] and (b) there seems to be a relation between the structures of crystalline boric oxide and cubic metaboric acid[263], appear significant in that $3B_2O_3$ groups are equivalent to two boroxole rings which, when joined by two oxygen links as suggested earlier[260], have an element of cubic structure in them. No attempts have as yet been made to determine the structure of the dense monoclinic, or β, form of crystalline boric oxide obtainable on application of high temperatures and pressures.[43]

Boric Oxide Vapour

The study of boric oxide in the vapour phase also has been pursued. After B_2O_3 was shown to be the predominant species (a) by mass spectrometric techniques[266], (b) in effusion and flow vapour pressure studies[144] and (c) from the result of a determination of its average molecular weight[55], the presence of two boron atoms in the molecule was confirmed in an infra-red emission study and a structural formula of a bipyramid (D_{3h} model) was assigned to it.[267] Objections to this configuration of the B_2O_3 molecule in the vapour phase were raised[268–9] and much infra-red[19, 268, 270] and electron diffraction evidence[271–3] was produced in favour of the C_{2v} symmetry which allows the presence of two double boron to oxygen bonds:



There is general agreement on the bond lengths, viz. 1·36 Å for the B—O bond and 1·20 Å for the B=O bond.[270] The B—O—B angle given originally as 95° on the basis of electron diffraction data[271] was amended later to 120° on the basis of evidence obtained in an infra-red study by a 'matrix isolation technique' which allows the trapping and study of molecules at lower temperatures.[270] It remains

Table XII.—Lengths and Strengths of Bonds in Boric Oxide

Bond	Length, Å	Strength, kcal mole^{-1} (kJ mole^{-1})	Year	Reference
B—O	1·39	—	1936	206
	1·35	—	1946	275
	—	119 (498)	1947	106
	—	100 (418)	1956	229
	1·38	—	1957	225
	1·37	—	1958	207
	1·36	—	1960	271
	1·36	—	1962	270
	1·36	123 (514)	1963	276
	—	125 (522)	1965	277
B=O	1·20	—	1958	278
	1·20	—	1960	271
	1·20	—	1962	270
	—	200 (936)	1963	276
O ↔ O (distance)	2·39	—	1957	225
	2·37	—	1958	207

to be seen whether a recent opinion (1965) in favour of the D_{3h} symmetry[274] will modify the general confidence in the correctness of the V-shape interpretation of the structure of the gaseous molecule.

To supplement the data on bond strengths and lengths quoted in the above discussion, the results reported by various authors up to 1965 are summarized in Table XII.

A formula relating the boron–oxygen bond energy to the length of the bond was proposed:

$$\log D = 3{\cdot}5244 - 1{\cdot}055r,$$

where D is energy in kcal mole^{-1} and r is the bond length in Å. For the double B=O bond, which is 1·20 Å long, the formula gives a bond energy of 181 kcal mole^{-1} (755 kJ mole^{-1}), whereas a value of 200 kcal mole^{-1} (936 kJ mole^{-1}) was calculated from data available for the gaseous B_2O_3 molecule.[276]

Reviews of the theories of structure of boric oxide were made by Warren *et al.* up to 1936[206], Weyl in 1948[182, 283], Fajans and Barber in 1952[215], Gmelin in 1954[284], Kemp in 1956[285], Mackenzie in 1956[229], 1960[227] and 1962[286], Krogh-Moe in 1959[236] and in 1966[287], Pascal *et al.* in 1961[288], Young and Westerdahl in 1961[256], Borelli and Goug-Jen Su in 1963[258], Nies and Campbell in 1964[289] and Rawson in 1967.[290] The controversial issues involved in the structure of gaseous boric oxide were discussed in detail by Hanst *et al.* in 1965.[274]

In concluding this chapter it may be mentioned that the green flame coloration observed with boron compounds is not due to the presence of B_2O_3 molecules as was sometimes thought (e.g.[144]), but to BO_2 molecules.[141, 279–282]

CHEMICAL PROPERTIES OF BORIC OXIDE

Boric Oxide is amphoteric, i.e. capable of entering into compounds with bases, e.g. $CaO + B_2O_3 \rightarrow Ca(BO_2)_2$, and with acids, e.g. $B_2O_3 + P_2O_5 \rightarrow 2BPO_4$. The acidic character is, however, predominant[291] and distinctly more pronounced than in aluminium oxide.[292]

Reduction of Boric Oxide

Since reduction of boric oxide entails rupture of the very strong boron–oxygen bond, it can be achieved only by using very active reducing agents. Thus, whereas the action of hydrogen gas at temperatures of about 830–1130°C on a mixture of boric oxide and boron gives boroxine, $B_3O_3H_3$[293–4] and some hydroxyboroxine, $B_3O_4H_3$[293], boric oxide can be reduced to elemental boron by hydrogen in an electric arc. The higher effectiveness of this reducing agent is attributed to the presence of H_2^+ and H^+ ions.[295] Hydrogenation of boric oxide can be effected with the gas at 500–700°C in the presence of $NaAlCl_4$; the mixture of products contains diborane, B_2H_6.[296] If the reaction is carried out at 750 atm and above 150°C in the presence of aluminium chloride, a 40–50% yield of diborane can be obtained; in the presence of secondary or tertiary alkylamines the products are amine boranes, aminoboranes and borazines.[297] A reduction of boric oxide can be effected by heating it in vacuum at 800–900°C with lithium hydride[298] and a 60% yield of sodium borohydride, $NaBH_4$, can be obtained by its reaction with sodium hydride at 330–350°C.[299] A 70% yield of sodium borohydride was claimed in a patent describing a reaction at 450°C between metallic sodium, boric oxide and hydrogen under 4 atm pressure in the presence of silica.[300] Boric oxide can also be reduced with calcium hydride at temperatures above 600°C; the reactions $B_2O_3 + 3CaH_2 \rightarrow 2B + 3CaO + 3H_2$ and $6B + CaH_2 \rightarrow CaB_6 + H_2$ are rapid at 1200°C, but in the presence of excess of B_2O_3 calcium hexaborate, $CaO.3B_2O_3$, is formed.[301] The product of reduction of boric oxide with elemental boron obtained on heating the reactants at 1350°C in a tantalum crucible under vacuum was said to be the suboxide BO which has density[302] about 1·765 g cm^{-3}; but in another study no compound BO was found in the gaseous phase over a mixture of liquid boric oxide with solid boron kept at temperatures of the order of 1000–1200°C; the most abundant of the suboxides present was B_2O_2.[303] The rate of reduction of boric oxide with carbon becomes appreciable at 950°C; active carbon reacts more readily than graphite whilst silica has an inhibiting effect on the reaction.[304] Below about 1280°C the main reaction is given by: $B_2O_3(l)+3C(s) \rightarrow 3CO(g)+2B(s)$, and above about 1330°C gaseous B_2O_2 is found amongst the products according to the equation: $B_2O_3(l)+C(s)= B_2O_2(g)+CO(g)$.[305–6] Electrolytic reduction of boric oxide in the presence of carbon may be used for the manufacture of elemental boron, the reaction being: $2B_2O_3+3C \rightarrow 4B+3CO_2$.[307] Although reduction of mixtures of boric oxide with an oxide of Group IVA elements is a standard method of preparing borides, e.g. titanium diboride[308], the products of reduction of mixtures of boric oxide and the oxides of metals of Group IIIB (Ga, In, Tl) and IVB (Ge, Sn, Pb) with carbon do not include borides.[309] Thin coatings of boric oxide on graphite, possibly reinforced by the solid products of reactions between the oxide and the carbon, suppress effectively the oxidation of graphite by atmospheric oxygen at high temperatures.[310–12] A concise review and discussion of a number of reduction reactions of boric oxide with, *inter alia*, elemental carbon, boron and boron carbide, was published in 1965.[313] The action of hydrogen on a mixture of boric oxide with boron, carbon or boron carbide at 1000°C gives rise to formation of diborane and related hydrides.[314] Reduction of boric oxide with elemental boron and lithium at temperatures from 1200 to 1800°C and pressures from 50,000 to 75,000 atm has been shown to yield the suboxide B_2O.[315] Boric oxide is reduced[316] at elevated temperatures by alkali metals, alkali-earth metals and aluminium (Mellor, V, 44) to yield amorphous boron of varying purity. When aluminium powder is used the separation of the liquid from the solid products of reaction is facilitated by inclusion of up to 20% of copper or magnesium powder, the presence of either of which brings about a lowering of viscosity of the liquid phase.[317] Alternatively, the separation of the products of reaction by acid treatment is facilitated by the inclusion of calcium oxide with the reaction mixture.[318] When the reduction of boric oxide is carried out in the presence of a fluoride, e.g. PbF_4, the product is boron trifluoride.[319] The most convenient and most frequently used metal for the reduction of boric oxide is magnesium.[320–30] The chief reaction producing elemental boron is given by: $B_2O_3+3Mg \rightarrow 2B+3MgO$. The contaminants include always boron suboxides and magnesium boride(s), and, when an excess of boric oxide is used, magnesium borate(s).[330] The product of reaction of boric oxide with manganese at 900°C is manganese boride which is ferromagnetic.[331] The capacity of metals and carbon to reduce boric oxide undoubtedly plays an important part in the boriding of carbon steels.[332] Boric oxide does not react with the noble metals gold and platinum and their lattice spacings are scarcely altered on dispersion in boric oxide glass.[333]

The surface of boric oxide is not markedly active in promoting the recombination of hydrogen atoms in contact with it, and there is relatively little enhancement of activity with rise of temperature.[334] The presence of the oxide in contact with a mixture of hydrogen and oxygen gas has no significantly inhibitive effect on the rate of the explosive reaction between the two gases, there being no evidence for a chain breaking factor above 520°C.[335] It is, however, possible that, indirectly, boric oxide may affect the rate by interacting with water, itself a known inhibitor of the hydrogen–oxygen reaction.[336]

Oxygen gas at 1 atm pressure reacts with boric oxide at 1200°C according to the reaction: $B_2O_3+\frac{1}{2}O_2 \rightarrow 2BO_2$. The product gives rise to colour bands at wavelengths 5470 and 5200 Å.[337–9]

Reaction with Water

Boric oxide reacts readily with liquid water and water vapour to form boric acid at ambient temperatures: $B_2O_3+3H_2O \rightarrow 2H_3BO_3$. The reaction is accompanied by liberation of a considerable amount of heat, i.e. about 18·3 kcal mole^{-1} (76·5 kJ mole^{-1}) crystalline B_2O_3.[104,298] Attack by water on the dense monoclinic or β-B_2O_3 form is relatively slow.[43] Above about 135–140°C the product of the action of water vapour on solid boric oxide is metaboric acid[20,120,340–2]: $B_2O_3(s) + H_2O(g) \rightarrow 2HBO_2(s)$. At 800–1200°C the reaction: $B_2O_3(l) + H_2O(g) \rightarrow 2HBO_2(g)$ is endothermic, 84·6 kcal mole^{-1} (353 kJ mole^{-1}) B_2O_3 being absorbed; when both reactants are in the gaseous state 2·8 kcal mole^{-1} (11·7 kJ mole^{-1}) B_2O_3 are liberated. A study of gaseous species in thermodynamic equilibria with boric oxide and water vapour at these temperatures showed the presence of the ions H_2O^+, HBO_2^+, $H_3BO_3^+$ and $(HBO_2)_3^+$; at 1178°C the HBO_2^+ ion is by far the most abundant of the borate species with less than 1% of each of the remaining two.[342] The solubility of water vapour in molten boric oxide decreases with increasing temperature; at a fixed temperature and pressure it is proportional to the square root of the partial pressure, and at 1000°C and 1 atm it amounts to 2 mole %. A proportion of the water vapour dissolving in boric oxide reacts with it to form hydroxyl ions.[343] A comprehensive review of the reactions of boric oxide with water vapour at high temperatures was published in 1963.[21]

Reactions with Halogens

Boric oxide reacts readily with fluorine (Mellor, V, 43) to form the volatile boron trifluoride; the reaction can be utilized in the removal of residual fluorine from hydrocarbon oils processed in the presence of hydrofluoric acid.[344] Complete displacement of oxygen from boric oxide with fluorine can be achieved by using bromine trifluoride.[345] The action of boron trifluoride on boric oxide at temperatures above 100°C gives rise to the formation of the trimeric boron oxyfluoride[346–8], according to: $B_2O_3(s \text{ or } l) + BF_3(g) \rightarrow (BOF)_3(g)$. The reaction is endothermic with a requirement of 4·2[347] or 2·4 kcal mole^{-1} (17·5 or 10·0 kJ mole^{-1}) $(BOF)_3(g)$[348] when starting with the liquid boric oxide. At higher temperatures permitting an additional supply of about 131 kcal[347] the product is the monomer BOF, $B_2O_3(l) + BF_3(g) \rightarrow 3BOF(g)$.[347–9] Hydrofluoric acid converts boric oxide into the fluoride BF_3 (Mellor, V, 43); the action of 40% aqueous solution of the acid was found to yield $BF_3.2H_2O$, whereas dry hydrogen fluoride is believed to give $HBF_2(OH)_2$.[346,350] A study of the system HF–B_2O_3–(BF_3)–H_2O has been made.[351]

Chlorine does not act on boric oxide at temperatures below about 900°C[352], but the presence of carbon facilitates the reaction: $B_2O_3 + 3C + 3Cl_2 \rightarrow 3CO + 2BCl_3$ to such a degree (Mellor, V, 43) that it has become the basis of commercial methods of production of boron trichloride; a few variants in the technique have been the subjects of patents.[353–5] Chlorination commences at about 350°C but in practice temperatures of 850–900°C are used to speed up the process.[356] In analogy to boron trifluoride, the trichloride reacts with boric oxide to give the trimer $(BOCl)_3$ at temperatures between 500 and 600°C; the monomer BOCl is formed at, and above, 1000°C.[357–61] In a nuclear magnetic resonance study of the BCl_3–B_2O_3 system using the ^{11}B isotope the details of the structural units could not be established with precision, but the relative scarcity of end groups is interpreted as being an indication of extensive branching and ring formation in the system.[362] Hydrogen chloride and hydrogen bromide are not significantly reactive towards boric oxide at ambient temperatures (Mellor, V, 43). Sulphur monochloride, S_2Cl_2, was thought to have no action on boric oxide (Mellor, V, 44), but more recently it was shown that it quantitatively displaces oxygen from the oxide.[363] With thionyl chloride the reaction: $B_2O_3 + 3SOCl_2 \rightarrow 2BCl_3 + 3SO_2$ can be induced in a bomb at 150–300°C.[364]

Reactions of boric oxide with halogen salts at high temperatures were explored with a view to obtaining methods for the production of boron halides. There is no doubt about the relatively free evolution of boron trifluoride from a mixture of boric oxide and calcium fluoride heated above 900°C[365], but the corresponding reaction between boric oxide and calcium chloride is considerably slower.[366] The claim that reactions take place between boric oxide and alkali-metal halides may be justified in the case of fluorides, since a 54% yield of BF_3 was obtained from a mixture of about 7·3 parts of boric oxide and about 2·7 parts of lithium fluoride heated to 800–1000°C[367], but the yields with chlorides are too low to be of practical interest.[289] The conclusions of a recent study were that whereas boric oxide reacts with the chlorides of carbon, silicon, phosphorus and sulphur to yield boron trichloride, no detectable quantities of this product were obtained on heating boric oxide with the chlorides of sodium, calcium, mercury, zinc, iron and arsenic or with hydrogen, ammonium, methyl, phosphoryl and sulphonyl chlorides or phosgene.[368] As might be expected, a reaction between boric oxide and a halide salt can often be facilitated by the presence of sulphuric acid, e.g.

(i) $2B_2O_3+2Na_3AlF_6+9H_2SO_4 \rightarrow 4BF_3+6NaHSO_4+Al_2(SO_4)_3+6H_2O$

(ii) $B_2O_3+3CaF_2+3SO_3 \rightarrow 2BF_3+3CaSO_4$

A comprehensive review of reactions of boric oxide with fluorides in the presence of acids can be found in a work on boron trifluoride published in 1949.[369] Reactions between boric oxide and halides can sometimes be induced by simultaneous application of heat and pressure, e.g. a 7·5% yield of boron trichloride was obtained by heating 3 parts of boric oxide with 11 parts of aluminium chloride in a steel bomb for 16 hr at 350°C.[366] Records of observations of reactions of boric oxide with aluminium halides in the vapour phase are found in recent papers.[370–2] If boric oxide is heated with an aluminium halide in an atmosphere of hydrogen at high pressures (e.g. 750 atm) the products are boron hydrides.[373] Nitrogen trifluoride reacts with boric oxide in a nickel tube at 615°C to yield a mixture of products[374]:

$$B_2O_3+3NF_3 \rightarrow 2BF_3+3NOF$$
$$B_2O_3+6NOF \rightarrow 2BF_3+3NO+3NO_2$$
$$BF_3+NOF \rightarrow NO^+(BF_4)^-$$

Boric Oxide–Halogen Salt Equilibria

Considerable attention has been given to the structural and chemical relationships in melts of boric oxide with halogen salts. In the course of a study of the ternary systems $NaF–KF–B_2O_3$ and $KF–KCl–B_2O_3$ glassy phases were observed in the binary systems $NaF–B_2O_3$, $KF–B_2O_3$ and $KCl–B_2O_3$ when the proportion of the halide did not exceed 55, 50 and 20 mole % respectively.[375] The capacity of boric oxide for dissolving relatively large proportions of fluorides is important in the preparation of special glasses.[376] When in 1948 the results of *X*-ray studies on alkali halide–boric oxide glasses were claimed to indicate the presence of 'crystallites' of undissociated halide salts[377], an attempt was made to explain the observations by suggesting that the 'crystallites' appeared only when the alkali halide was present in excess of that which is soluble in boric oxide.[378] The explanation is probably valid if by 'crystallites' literally small crystals of alkali halides are meant; but if there is *X*-ray evidence showing that, although the bonds between the atoms in a molecule of metal halide in boric oxide glass may be weakened[379], the essential features of its crystalline structure persist at concentrations as low as, for instance, 3·5% NaCl[380], then such evidence cannot be dismissed without further study. The subject deserves more attention and, if pursued, may add to knowledge of the structure of boric oxide itself. It has been suggested that whereas boric oxide may ionize in molten cryolite[381] and in sodium fluoride[382], there is no ionization in the cryolite–sodium fluoride eutectic[383] or in sodium chloride.[384] In a recent study of the system $LiF–BaF_2–B_2O_3$ the compounds $LiF.B_2O_3$, $3BaF_2.B_2O_3$, $2BaF_2.3B_2O_3$ and $BaF_2.4B_2O_3$ were claimed to have been found.[385]

Reactions with Sulphur and Sulphur Trioxide

Gaseous sulphur at about 1000°C does not, and indeed cannot, react with boric oxide.[386, 387] There has been disagreement as to whether boric oxide reacts with sulphur trioxide (Mellor, V, 44). That boric oxide stabilizes liquid sulphur trioxide is claimed in the patents covering such use.[388–91] Following a study of absorption of labelled sulphur trioxide in a boric oxide-glass melt, slight and only superficial fixation of the trioxide was reported[392], but more recently the existence of $B_2O_3.2SO_3$ as the only compound in the B_2O_3–SO_3 system was claimed. This compound was prepared by heating boric oxide with excess of sulphur trioxide in a sealed tube to temperatures above 150°C for 12 hr; at lower temperatures only solid solutions of the two components were obtained.[393] The results of cryoscopic and conductivity studies of solutions of boric oxide in sulphuric acid indicated that the reaction: $B_2O_3+9H_2SO_4 \rightarrow 2B(HSO_4)_4^- + 3H_3O^+ + HSO_4^-$ occurred. With oleum formation of a strong acid, $H[B(HSO_4)_4]$ that can be titrated with potassium bisulphate to give $K[B(HSO_4)_4]$ was reported.[394] In disulphuric acid the complex formed is $H[B(HS_2O_7)_4]$.[395] In the system Na_2S–B_2O_3 glass formation was found to occur within the range 64·0–78·1% boric oxide and the existence of the compounds $Na_2S.2B_2O_3$, $Na_2S.3B_2O_3$ and $Na_2S.4B_2O_3$ in analogy with sodium borates has been suggested as likely.[396] Boric oxide reacts with the $S_2{}^-$ ion in molten sodium fluoride to give the BO_2^- and BOS^- ions.[382] Boric oxide was observed to increase the strength of anhydrous calcium sulphate binder ('anhydrite'), but the mechanism of reactions involved has not been studied.[397]

Reaction with Ammonia

Ammonia reacts with heated boric oxide to form boron nitride[398] (Mellor, V, 44); a reaction temperature of about 900°C is recommended in a process for the production of boron nitride on the commercial scale.[399] Hexagonal boron nitride can also be obtained from the reaction of boric oxide with sodium amide: $B_2O_3+3NaNH_2 \rightarrow 2BN+NH_3+3NaOH$; the reaction can be carried out at 210°C or at lower temperatures (e.g. 165°C) in the presence of a large excess of sodium hydroxide.[400]

The solubility of boric oxide in nitric acid is governed by the amount of water present and is highest, viz. 25%, in 91% HNO_3 decreasing to 6% in 100% HNO_3.[401]

Reactions with Silica

Reactions of boric oxide with silica have been given considerable attention, the interest springing mainly from the uses of the two oxides together in glass, ceramics and vitreous enamels. It is, however, particularly difficult to study this system. Mixtures of the oxides in the molten state are very viscous so that long heating times are required for the establishment of equilibria, and if the heating is carried out in vessels open to the atmosphere absorption of water and loss of the boric oxide through volatilization tend to affect the accuracy of the results. Attempts at producing phase diagrams and establishing the liquidus curve were made with varying and often conflicting results. Early this century silica was thought to be insoluble in boric oxide and the formation of insoluble compounds of various B_2O_3:SiO_2 ratios was proposed. However, there was no confirmation of immiscibility in studies carried out between about 1927 and 1938.[58, 402–4] In 1953 it was claimed that boric oxide does not mix completely on a micro-dimensional scale with silica since aggregates 16–20 Å in diameter persist at temperatures as high as 1650°C.[405] The existence of compounds in the system was again suggested more recently on the basis of observations of breaks in the curves of various physical properties of boric oxide–silica glasses[406–7], though breaks in property–composition curves are not necessarily a proof of compound formation.[408] A comprehensive review of earlier theories was published in 1965[409] as well as conclusions given from the results of a study carried out on mixtures heated in sealed platinum capsules and examined under xylene to prevent hydration. The conclusions were that there is no evidence for either liquid immiscibility or compound formation in the system, but the problem is by no means finally settled and the search for more information on this interesting topic may be expected to continue.

The results of practical determinations of the relative rates of reactions between various oxides and silica at elevated temperatures showed boric oxide to react more slowly than the alkali metal oxides and lead monoxide, but faster than alkaline-earth metal oxides and the oxides of zinc, titanium, aluminium and zirconium.[410–11] In reactions of boric oxide with solid silica the rate of reaction is governed by the activation energy of diffusion of boric oxide.[412] The dissolution of quartz in molten boric oxide was quoted as an example of dissolution in viscous systems in which both diffusion and free convection control the rate of dissolution.[413] Boric oxide reacts in the gaseous phase with silicon monoxide to give fibres containing silicon crystals.[414] Boric oxide has a profound effect on the polymorphic changes occurring during heat treatments of dicalcium silicate, $2CaO.SiO_2$[415–20] and tricalcium silicate[421–3], but the mechanism of its action is not clear; some of the proposed reactions[416, 422] appear to be unlikely. Examinations of considerably higher precision than those hitherto undertaken are required to elucidate the mode of action of the oxide on the setting of cements.

Reaction with Phosphorus Pentoxide

Phosphorus pentoxide is very soluble in boric oxide at 1200°C. From the melts of the two oxides the chemically stable boron phosphate, BPO_4, crystallizes on cooling.[404] Boron phosphate also appears to be a primary phase over a considerable area of the triangle B_2O_3–BPO_4–SiO_2 in the three-component system, i.e. it can be crystallized from melts containing silica and/or excess of boric oxide.[424]

Reactions with Metal Oxides

Liquid boric oxide is remarkably reactive towards metal oxides[425] and its powerful solvent action on them has been the basis of its many applications in metallurgical processes. Following the results of observations reported by earlier workers (Mellor, V, 41) systematic re-examination of solubility data was carried out in 1938[404] with the following conclusions:

1. All alkali metal oxides (Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O) as well as cuprous and thallous oxides are soluble in all proportions in boric oxide at 1200°C. On cooling, crystalline borates, glasses, or mixtures of both are obtained, rapid cooling and high boric oxide content favouring glass formation. The solubility of silver oxide, Ag_2O, is limited in that at concentrations above 61% by weight of the melt metallic silver separates out. At temperatures below about 1000°C, melts with cuprous oxide absorb oxygen from the atmosphere and the cupric oxide formed causes separation of the melt into two liquid layers. In the absence of air the cuprous oxide in the melt disproportionates on slow cooling into cupric oxide and elemental copper.
2. Alkali-earth metal oxides (MgO, CaO, SrO, BaO), zinc and cadmium oxides, manganous oxide and oxides of iron(II), cobalt(II) and nickel(II) on dissolving in boric oxide cause separation of the liquid into two layers; an upper layer contains small proportions of the metal oxide (e.g. 0·63% by weight of MgO, increasing with molecular weight to 7·35% by weight for BaO) and a lower layer with a large proportion (e.g. 34·2% for MgO and 30·4% for BaO) of the metal oxide in solution. The relationship between molecular weight and solubility is well illustrated by the fact that whereas the solubility of the lightest of oxides of Group II metals, viz. beryllium oxide, is limited to 0·19% by weight, there being no separation of the liquid into two layers, plumbous oxide is soluble in all proportions in boric oxide at 1200°C. Up to about 5% by weight of mercuric oxide can be dissolved in boric oxide at 600–650°C, but at higher temperatures mercuric oxide decomposes. Mercurous oxide at similar temperatures and in the absence of air disproportionates into mercuric oxide and mercury metal before going into solution as the higher oxide. On dissolving ferrous oxide in boric oxide at 1200°C part of the metal oxide disproportionates, in the absence of air, into

ferric oxide and metallic iron with precipitation of the latter in the lower layer. Cupric oxide, however, is reduced quantitatively to cuprous oxide in boric oxide at temperatures above 900–1000°C.

3. The solubilities of alumina and chromic oxide in boric oxide at 1200°C are 1·05 and 1·72% by weight respectively. Ferric oxide, even in presence of atmospheric oxygen, is partially reduced so that a boric oxide melt at 1200°C contains 5·38% by weight of Fe_2O_3 and 0·75% by weight of FeO. The rare-earth oxides, lanthanum oxide (La_2O_3) and cerium oxide (Ce_2O_3), give rise to two-layer formation with small proportions (about 1·5 and 3·0% respectively) of the oxides dissolved in the upper layer and large proportions (about 60% by weight) in the lower layer. The arsenic group oxides (As_2O_3,Sb_2O_3 and Bi_2O_3) dissolve in boric oxide at 1200°C in all proportions.
4. The solubilities of dioxides of titanium, zirconium, molybdenum, tin, tungsten and thorium in boric oxide at 1200°C decrease in the order $TiO_2 > ZrO_2 > MoO_2 > SnO_2 > WO_2 > ThO_2$, i.e. with diminishing acidity, from about 5% to about 0·5% by weight of melt. Cerium dioxide in excess of boric oxide at 1200°C loses oxygen rapidly and dissolves as Ce_2O_3.
5. Typical of the M_2O_5 oxides, vanadium pentoxide is soluble in all proportions in boric oxide at 1200°C.
6. The solubility of uranium oxide (U_3O_8) in boric oxide at 1200°C is 3·2% by weight of the melt. The oxide precipitates from the solution on cooling.
7. Oxides of the MO_3 type are very soluble in boric oxide. Molybdenum trioxide is soluble in all proportions at 1200°C and tungsten trioxide is soluble to about 71% by weight of melt. The solubility of tungsten trioxide as a function of temperature gives a curve of a shape typical for solutions of salts in aqueous solvents. Similar curves are also obtained with other partially soluble metal oxides.[404, 426]

It should be mentioned that the solubility data quoted above for the upper layers, in cases of partially soluble oxides which give rise to the formation of two immiscible layers, may be unreliable in that it appears doubtful whether sharp distinction between the layers is possible. Results of more recent work[427] indicate that the upper layer, at least in some immiscible systems, consists of pure boric oxide since the surface tension is that of boric oxide. Furthermore, it has been proposed that the tendency to immiscibility is also exhibited even by the alkali-metal oxide–boric oxide melts, and the size of the 'immiscibility gap' (range of concentrations of the solute within which the surface layer consists of pure boric oxide) for the partially miscible oxides is governed not by the molecular weight of the metal oxide but by the ionic potential, i.e. charge to radius ratio, of the metal; the trend is shown in Table XIII.

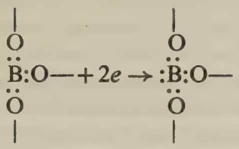
Table XIII.—Immiscibility in Metal Oxide–Boric Oxide Systems at 900°C and Ionic Potential of Metals[427]

Metal	Ionic potential,* z/r	'Immiscibility gap',† mole % metal oxide
K	0·75	0
Na	1·02	0
Li	1·28	0
Ba	1·40	16
Pb	1·51	19
Sr	1·57	21
Ca	1·89	27
Zn	2·41	49
Mg	2·56	50

* Charge to radius ratio: z = valence; r = ionic radius (Å).

† Range of concentrations within which a surface layer of pure boric oxide is formed.

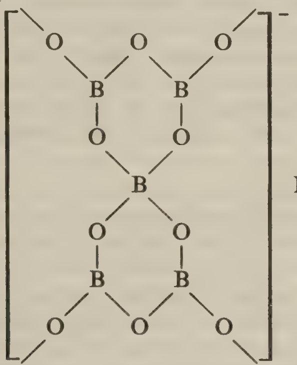
The reactions and the strong solvent action of boric oxide towards metallic oxides are best interpreted in terms of its acidity[291, 428] in the sense that it is a strong Lewis acid[429, 430] with a marked capacity for forming a bond by accepting one pair of electrons:



$$\begin{array}{c} | \\ \mathrm{O} \\ \cdot\cdot \\ \mathrm{B{:}O}- \\ \cdot\cdot \\ \mathrm{O} \\ | \end{array} + 2e \rightarrow \begin{array}{c} | \\ \mathrm{O} \\ \cdot\cdot \\ \mathrm{{:}B{:}O}- \\ \cdot\cdot \\ \mathrm{O} \\ | \end{array}$$

The acceptance of one pair of electrons is tantamount to a change from triangular to tetrahedral bond configuration as illustrated by the examples of sodium pentaborate and borax:

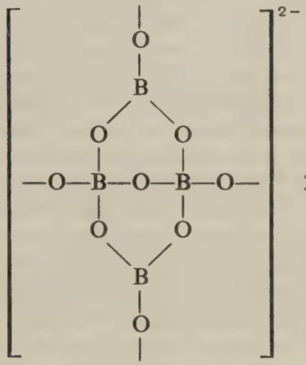
$2{\cdot}5B_2O_3 + 0{\cdot}5Na_2O =$



Na^+

Anhydrous sodium pentaborate

$2B_2O_3 + Na_2O =$



$2Na^+$

Anhydrous borax

Recent studies of reactions of boric oxide include those with the oxides of vanadium[431], zinc[432], zirconium[433] and thorium[434], but most of the effort has been directed towards elucidation of the mechanisms of reactions with iron oxides and the oxides on surfaces of high temperature alloys. Boric oxide in close contact with ferric oxide slows down the rate of reduction of the latter by hydrogen[435] and it has been reported as accelerating the rate of oxidation of reduced iron catalysts at temperatures from 150 to 600°C.[436] At temperatures in the range 850–1000°C an addition reaction between the boric and ferric oxides yields ferric borate. This is readily reduced to ferrous borate by carbon but below 1000°C the reduction does not proceed further so that significant amounts of boron, boron carbide or iron boride are not produced.[437] The low surface tension of molten boric oxide promotes ready wetting of metal surfaces and, provided that a sufficient proportion of the oxide is added to form and maintain a continuous coating, the surfaces are effectively protected against oxidation during heat treatments.[438–42] If however iron, cobalt or nickel-base alloys are subjected for prolonged periods (e.g. 100 hr) to frequent cycling comprising alternate immersion in molten boric oxide at temperatures of about 1100°C and exposure to the atmosphere, the oxidation of the alloys is markedly accelerated.[443–5] This might be expected bearing in mind the likely combined effects of its solvent action and increasing volatility above 1100°C. These effects have been summarily ascribed to 'corrosion of metals and alloys by boric oxide', whereas the proportion of damage done through direct reaction resulting in formation of, for instance, borides[445] must be minor and secondary to that brought about by the oxidation process. Direct reaction, such as there is, has been shown to be enhanced by the presence of carbon, aluminium, titanium and manganese in the alloys[443, 445] whereas the presence of silicon is beneficial.[444] Although the resistance to oxidation of metals completely immersed in or having surfaces completely covered by boric oxide is better than that of the same metals in air, partially immersed metals or partially covered surfaces, as in containers holding molten boric oxide, are open to attack at the liquid/air interface. Also, a rapid reaction over the whole surface area of contact can be expected if a container like a crucible is made of an oxide. Thus magnesia and zirconia crucibles are destroyed within 15 min of contact with boric oxide at 1250°C; alumina crucibles are, however, not rapidly attacked at this temperature.[446]

A very useful collection of phase diagrams of systems comprising boric oxide and one, two or three metal oxides appeared in 1956[447] and a complementary set was added in 1959.[448] The latest and most comprehensive collection of such data was published in 1964.[449] This includes (apart from a tentative plot of pressure/temperature relationships for the α and β crystalline forms of boric oxide): 17 diagrams of two-component systems (i.e. B_2O_3 with Al_2O_3, BaO, Bi_2O_3, CaO, CdO, CoO, Cs_2O, H_2O, K_2O, La_2O_3, Li_2O, MgO, MnO, Na_2O, PbO, ThO_2 and ZnO); 19 diagrams of three-component systems (i.e. B_2O_3 with Al_2O_3–Li_2O, Al_2O_3–SiO_2, BaO–SiO_2, CaO–SiO_2, CdO–ZnO, H_2O–K_2O, H_2O–Li_2O, H_2O–Na_2O, K_2O–Na_2O, K_2O–P_2O_5, Li_2O–P_2O_5, Li_2O–SiO_2, NaF–Na_2O, Na_2O–SiO_2, P_2O_5–SiO_2, PbO–SiO_2, PbO–TiO_2 and SiO_2–ZnO); 5 diagrams of four-component systems (i.e. B_2O_3 with Al_2O_3–Li_2O–SiO_2, BaO–PbO–TiO_2, CaO–Na_2O–SiO_2, CrO_3–K_2O–Na_2O and K_2O–Li_2O–WO_3); and 1 diagram of a six-component system (B_2O_3–Al_2O_3–H_2O–MgO–Na_2O–SiO_2). All these diagrams are provided with references to original papers. More recent studies were reported in the literature on the systems comprising B_2O_3 with CaO–P_2O_5[450], Na_2O–SiO_2[451], Sc_2O_3[452], SrO[453], PbO[454, 455], Na_2O–PbO[456] and BaF_2–Na_2F_2.[457] *X*-Ray and diffraction examination has also been made of thin films of Fe_3O_4–B_2O_3 mixtures deposited from the vapour phase.[458]

Boric oxide displaces carbon dioxide from sodium carbonate when mixtures of the two are heated above 350°C. In the presence of sufficient carbonate at temperatures above 700°C the compound $3Na_2O.B_2O_3$ was claimed to be formed[459], but such a compound has never been isolated and its existence in the solid state remains doubtful. At high pressures considerable amounts of carbon dioxide can be dissolved in molten boric oxide, e.g. the solubility of the gas at 2 kbar in boric oxide at 750°C is approx. 7 mole %, which is more than the solubility of nitrogen (approx. 4·5 mole %) or argon (approx. 6 mole %) under similar conditions.[460]

Molten boric oxide is a convenient solvent and medium for carrying out metal ion reduction and displacement reactions[426] but only a few of the possible applications have been examined. The reduction of cupric oxide with active carbon can be effected at 600°C; the dioxides of titanium and uranium are not so readily reduced and there is no evidence of reaction at 1000°C.[461] The growing of crystals of garnets and refractory oxides from boric oxide and systems based on it is being given a rapidly increasing amount of attention.[462] Subjects studied recently include preparation of crystals of: barium and lead titanates from solutions of PbO, BaO and TiO_2 in B_2O_3[463]; calcium zirconate, $CaZrO_3$, from melts including 4–24 mole % of B_2O_3[464, 465]; monocrystals of germanium oxide from B_2O_3 and from B_2O_3–KCl melts[466]; ferrites of the formula (MgO, MnO),Fe_2O_3 from boric oxide melt[467]; yttrium ferrite, $Y_3Fe_5O_{12}$, mixed yttrium/lanthanum ferrite and rare earth garnets of the general formula $M_3Fe_5O_{12}$ or $M_3Al_5O_{12}$ from solutions in B_2O_3–PbO mixed solvent[468–70]; yttrium iron garnet from B_2O_3–BaO solvent[471]; gallium iron oxide from B_2O_3–Bi_2O_3 melts[472] and garnets of the general formula $M_3M'_5O_{12}$, where M is yttrium or rare earth element and M′ is Fe, Al or Ga, from boric oxide–lead fluoride solutions.[473] Needle-shaped or fibre crystals of titania, zirconia and zircon can be obtained from boric oxide[474] or boric oxide–alkali metal oxide[475] media. Mixtures of lead and bismuth fluorides with small amounts of boric oxide are suitable for preparing crystals of hafnia, titania, thoria, ceria, yttrium chromate and alumina; the volatility of the fluoride component of the solvent at temperatures of the order of 1300°C is of assistance in these preparations.[476]

A separate chapter on the chemistry of boric oxide might be devoted to its use in electrochemical reactions, but since the object of studies carried out in this context was the preparation of elemental boron or of a metal boride the reader is referred to accounts in Sections C1 and C2. It will suffice here to summarize the salient features of these reactions. The conclusions of the work of one pioneer[477–81] in this field were that when a solution of metal oxide MO in a molten bath consisting of a mixture of boric oxide and a metal fluoride MF_2 at 1000–1200°C is electrolyzed then elemental boron, elemental metal M and a boride of the metal in varying proportions, depending on the conditions, are deposited at the cathode. With alkali metals low yields of impure boron are obtained, with alkali-earth (except magnesium) and rare-earth metals the product consists largely of a boride of the metal; in the case of magnesium a bath of the composition $2B_2O_3 + MgO + MgF_2$ yields a high proportion of elemental boron.[477] In addition to borides of alkali-earth and rare-earth metals, the borides of thorium, zirconium, chromium, manganese, titanium, vanadium, tantalum, tungsten, molybdenum, iron and nickel were identified as products of the electrolysis of the appropriate salt baths.[478–80] Improvements and variations in the electrolytic processes for the production of boron were elaborated and mostly patented.[482–90] The most notable advancement was made by substituting a mixture of potassium chloride and potassium fluoride for the mixture of MgO and MgF_2 in the original Andrieux process[482, 485–7] to yield boron of 94 to 97·5% purity. An alternative process claimed to yield similarly high-purity products is based on the electrolysis of mixtures of boric oxide with potassium fluoroborate[484, 488–90] or with potassium fluoroborate, potassium chloride and potassium hydrogen fluoride.[491]

Reviews of the inorganic chemistry of boric oxide, or at least of some aspects of it, were published in 1922 (Mellor, V, 41), 1948[182, 283], 1949[369], 1954[284], 1956[285], 1961[288], 1963[21] and 1964.[289]

The field of organoboron chemistry is very extensive and essentially outside the scope of this Section, but a number of important reactions of boric oxide with alcohols, Grignard reagents and other compounds are dealt with under the heading of 'Esters of Boric Acid', Section A17.

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SECTION A5

BORON SUBOXIDES

BY D. NICHOLLS

The following suboxides of boron have been reported: B_7O, $B_{13}O_2$, B_6O, B_3O, B_2O, B_4O_3, B_2O_2, $(BO)_n$, B_4O_5. Since each of these compounds might reasonably be called boron suboxide, this name is not appropriate for any one of the oxides and it will be necessary to refer to them by formula only in most cases.

THE OXIDES B_7O, $B_{13}O_2$ AND B_6O

Evidence for the existence of the first two of these oxides is conflicting and it may be that only one of the three exists. The suboxide B_7O was first reported by Weintraub[1] and by Kroll[2] over 50 years ago. These workers considered it to be present in the boron obtained by reducing boric oxide with magnesium, potassium or sodium. This oxide was often subsequently referred to as 'Moissan's boron' since he prepared his so-called amorphous boron by the magnesium reduction of boric oxide. Later Kahlenberg[3] claimed that B_7O is not a compound but a mechanical mixture of boron and a suboxide of formula B_3O. Chemical analysis of a sample prepared by Pasternak[4] gave a composition $B_{6\cdot6}O$ and crystallographic evidence indicated it to be the compound B_7O, which is orthorhombic. More recently[5] it has been suggested that the oxygen impurity in amorphous boron is present not as a boron suboxide but as $MgB_{30}O_{10}$.

One of the difficulties in establishing the formula of this oxide is the elemental analysis; often only boron has been determined and the residue assumed to be oxygen. This is particularly unsatisfactory, because not only is magnesium probably present as, e.g. MgB_6, but also because of the low atomic weight of boron compared with that of oxygen. La Placa and Post[6] re-examined the crystallographic data reported by Pasternak[4] for B_7O and concluded that the data can be indexed more satisfactorily on the basis of a rhombohedral cell with hexagonal cell constants, $a = 5{\cdot}37$ and $c = 12{\cdot}31$ Å. The appropriate formula of the suboxide is $B_{13}O_2$ which requires a calculated density of 2·80 compared to the experimental value for $B_{6\cdot6}O$ of 2·64 g cm^{-3}. A model of the structure of interstitial boron compounds such as B_4C, $B_{13}C_2$, $B_{13}P_2$ and $B_{12}S$ has been presented[7] in an attempt to explain the formation of compounds such as $B_{13}O_2$. Attempts to grow single crystals of $B_{13}O_2$ were unsuccessful.[8] A recent paper describes the preparation of B_7O by heating boron and zinc oxide at 1200–1550°C for four hours.[58] The product had an average Vickers hardness of 3820 kg/mm^2 (100 g load).

The oxide B_6O has been observed after the oxidation of boron in air and oxygen at above 1100°C and also as a product in the reaction of boron or silicon with boric oxide.[9, 10, 60] When a molecular mixture of boric oxide and boron corresponding to the formula B_6O is heated at 1500°C in helium under a pressure of 2 atm, the product contains B_6O and a small amount of unreacted boron. The major reaction for the formation of B_6O under these conditions is thus considered to be:

$$\tfrac{16}{3}B(s) + \tfrac{1}{3}B_2O_3(l) \rightarrow B_6O(s)$$

Chemical analyses of B_6O prepared from boric oxide and boron at various temperatures indicate no significant changes in composition; thus the solubilities of boron and oxygen in the suboxide must be low. Chemical analyses of B_6O prepared from boric oxide–silicon mixtures indicate either some solubility of silicon or the presence of SiB_6.

The physical and chemical properties of B_6O have not been fully established. The *X*-ray powder photograph has been recorded[9, 59, 60] and the density measured. For powdered samples, the density did not exceed 2·62 and the highest density found for hot-pressed B_6O was 2·588 g cm^{-3}. The hardness of B_6O is stated to be greater than that of boron carbide and titanium diboride. Above 1760°C, B_6O decomposes into crystalline boron and (presumably) oxygen. It is not attacked by hydrofluoric, hydrochloric or dilute nitric acid; it is oxidized when boiled with concentrated nitric acid, its oxidation resistance being slightly better than that of boron.

THE OXIDE B_3O

The existence of this oxide is doubtful. It is reported[3] to be one component of 'Moissan's boron' and is described as a brown powder not attacked by sulphuric acid or potassium hydroxide solutions but oxidized completely by nitric acid. Acid or alkaline potassium permanganate is reduced by B_3O, which becomes oxidized to boric oxide.

THE OXIDE B_2O

This oxide, which may be described electronically as an unsymmetrical analogue of graphite, has been synthesized using high temperatures and pressures. It may be prepared[11] by reducing boric oxide with boron or lithium, or alternatively by oxidizing boron with potassium chlorate. A convenient synthesis involves grinding boron and boric oxide together in the reaction ratio according to the equation:

$$4B + B_2O_3 \rightarrow 3B_2O$$

and then subjecting this mixture to 50,000–75,000 atm at 1200–1800°C. Pressures of about 120,000 atm have been used in unsuccessful attempts to synthesize a diamond-like form of B_2O.

The oxide B_2O is a light reddish-brown powder of density $2{\cdot}24 \pm 0{\cdot}04$ g cm^{-3}. *X*-Ray powder photographs indicate it to have hexagonal crystal symmetry with unit cell dimensions, $a = 7{\cdot}98$ and $c = 9{\cdot}09$ Å. These facts suggest a layer–lattice structure related to that of graphite.

THE OXIDE B_4O_5

Very little is known about this oxide. It is left as a white residue on evaporating a solution of the acid $H_{12}B_4O_6$ (obtained from the hydrolysis of magnesium boride, Mg_3B_2) in vacuo.[12] On addition of water it dissolves and forms a solution of the acid $H_2B_4O_6$. The action of heat on the ammonium salt of this acid regenerates B_4O_5[13]:

$$(NH_4)_2B_4O_6 \rightarrow B_4O_5 + H_2O + 2NH_3$$

BORON MONOXIDE, $(BO)_n$

The monoxide is the most commonly occurring and widely studied of the boron suboxides. It was originally identified spectrographically by Mulliken[14–16] in mixtures of oxygen and boron trichloride under high temperature or electrical discharge conditions. The molecule BO is isoelectronic with N_2^+, CN and CO^+ and has the electronic configuration $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p)^1$. The spectra of the molecule have been listed and reviewed by Herzberg.[17] The detailed spectrum of boron monoxide has also been discussed by several authors[18–28] and recently by Nicholls.[29, 30]

This molecule, however, is not as important in chemical reactions as the dimer B_2O_2. Two distinct routes to boron monoxide lead to two different solid modifications. These routes are (i) high temperature production of B_2O_2 gas, and (ii) dehydration of tetrahydroxydiboron, $B_2(OH)_4$.

High-temperature Routes to Boron Monoxide

OXIDATION OF BORON

The high-temperature form of boron monoxide was discovered in 1940 in a study of the reactions of boron with alumina and zirconium dioxide.[31] When boron reacts with alumina at 1300°C in vacuo, volatile suboxides of both boron and aluminium are evolved. With zirconium dioxide, ZrO_2, at 1800°C, however, only the boron is volatilized; by condensing the vapour, a bright brown transparent and amorphous sublimate is obtained with empirical formula BO. It is now known that boron monoxide vapour is present over many mixtures containing boron and a metal oxide at high temperatures. Thus magnesium oxide is reduced by boron at about 1100°C.[32]

$$2B + 2MgO \rightarrow B_2O_2 + 2Mg$$

and beryllium oxide is similarly reduced at about 1600°C.[33] Strontium oxide forms SrB_6 when heated with boron:

$$2SrO + 14B \rightarrow 2SrB_6 + B_2O_2$$

The boron monoxide may be contaminated with strontium at 1500–1700°C, where boride formation is slow.[34]

A convenient laboratory preparation of boron monoxide involves the reduction of boric oxide with boron at temperatures as low as 1050°C.[35] The carefully dried reaction mixture is heated in a tantalum crucible at a pressure of 10^{-4} mm Hg and the evolved monoxide vapour condensed on a water-cooled cold finger. The most favourable ratio of boron to oxygen in the reaction mixture is between 3:1 and 4:1:

$$2B + 2B_2O_3 \rightarrow 3B_2O_2$$

If temperatures much above 1350°C are used in this reaction, however, volatilized boric oxide begins to contaminate the product. Metal borates are similarly reduced by elemental boron.[36] The reactions of titanium and zirconium dioxides with boron and boron carbide are also suitable for the laboratory preparation of the monoxide.[37–8] The reactions begin at around 1000°C or lower, but temperatures in excess of 1050°C are more suitable for rapid sublimation of the monoxide at pressures of 10^{-3}–10^{-4} mm Hg. When the system has cooled down, the cold finger is removed under a stream of dry nitrogen and the amber glassy sublimate carefully scraped off (it is sometimes pyrophoric in air). In these reactions, the metal diborides are formed, the reaction stoicheiometries being, e.g. with titanium dioxide:

$$TiO_2 + 4B \rightarrow TiB_2 + B_2O_2$$
$$5TiO_2 + 4B_4C \rightarrow 5TiB_2 + 3B_2O_2 + 4CO$$

It is now apparent that $B_2O_2(g)$ is sufficiently stable to be formed when any involatile oxide is heated with boron in vacuo. The monomer, BO, is probably present in greater concentrations in the higher temperature reactions, e.g. BeO + B, and the reactions of zirconium or hafnium diboride with their dioxides have been suggested[32] as possible routes to the monomer.

REDUCTION OF BORIC OXIDE

As an alternative to the oxidation of elemental boron by metal oxides, boron monoxide can be prepared by reduction of boric oxide. Thermodynamic studies[39] on the carbon–boric oxide system led to the conclusion that the reaction:

$$B_2O_3 + C \rightarrow B_2O_2 + CO$$

should lead to production of the monoxide above 1330°C. Indeed, operating at 10^{-3} mm Hg the reduction of boric oxide by carbon proceeds slowly to give boron monoxide at 1150°C.[40–1] Higher yields of the monoxide are obtainable from this reaction at higher temperatures, but at 1550°C boron carbide is formed. In the presence of excess of boric oxide, however, boron carbide is also oxidized to the suboxide. Fairly pure boron monoxide is obtained in good yields by heating a 1:1 mixture of B_4C and B_2O_3 at 1250°C:

$$B_4C + 5B_2O_3 \rightarrow 7B_2O_2 + CO$$

Boric oxide is also reduced to the monoxide by titanium, titanium carbide and titanium diboride.[40–1] When titanium reacts with boric oxide at 1220°C, boron monoxide can be collected as a sublimate; the residue contains TiB_2 and α-Ti_2O_3:

$$3Ti + B_2O_3 \rightarrow TiB_2 + \alpha\text{-}Ti_2O_3$$

With excess of boric oxide and above 1200°C, the diboride reacts further according to:

$$2TiB_2 + 7B_2O_3 \rightarrow Ti_2O_3 + 9B_2O_2$$

thus accounting for the monoxide sublimate. The reaction of boric oxide with titanium carbide begins at about 1200°C and a fairly pure sample of boron monoxide can be collected using a temperature of 1400°C and a $TiC:B_2O_3$ ratio of 1:2.

Despite the many high temperature routes described above, the boron monoxide sublimates obtained are nearly always impure.[40–1] The boron analyses are usually lower than expected for the empirical formula BO. When starting with boric oxide, B_2O_3, the sublimates are nearly always contaminated to some extent with this material. In order to minimize such contamination, the starting materials must be absolutely anhydrous (the volatility of B_2O_3 is greatly increased in the presence of water vapour) and the reactions must be carried out below 1200°C at 10^{-3}–10^{-4} mm Hg. Under these conditions the more volatile B_2O_2 gas can be collected but the reactions tend to be slow and only small yields (about 0·5 g per run on the laboratory scale) can be collected. The reduction of metal oxides by boron might be expected to yield a boric oxide-free sublimate, but the analytical data for the products of these reactions are not significantly superior. The problem is largely one of apparatus design and experimental skill; induction heating of the reaction mixture is preferable to resistance heating since it uses a smaller hot zone and the sublimates are less liable to damage (disproportionation) by radiant heat. The best method would thus appear to be the reaction of pure boron with a metal oxide, e.g. TiO_2, the mixture being inductively heated in vacuo at 1600°C and the sublimate collected on a cold finger at room temperature.

Low-temperature Routes to Boron Monoxide

HYDROLYSIS OF METAL BORIDES

The hydrolysis of magnesium boride provides a variety of sub-boric acids.[12] The acids $H_2B_2O_2$ and $H_4B_2O_2$ are oxidized by iodine in aqueous solution to boron monoxide (which is then present as tetrahydroxydiboron, $B_2(OH)_4$). The ammonium salt of $H_4B_2O_2$, which is formulated as $(NH_4)_2B_2(OH)_2$, also yields the monoxide as a brown residue when heated in vacuo[13]:

$$(NH_4)_2B_2(OH)_2 \rightarrow B_2O_2 + 2H_2 + 2NH_3$$

The hydrolysis of the Be–B bond in Be_5B also produces[42] boron monoxide directly:

$$2Be_5B + 22H_2O \rightarrow B_2O_2 + 10Be(OH)_2 + 12H_2$$

FROM TETRAHYDROXYDIBORON

$B_2(OH)_4$ begins to evolve water at about 90° in vacuo and after several hours at 220° it is quantitatively converted to the monoxide[43]:

$$B_2(OH)_4 \rightarrow B_2O_2+2H_2O$$

Initially, tetrahydroxydiboron had to be obtained by hydrolysis of diboron tetrachloride, B_2Cl_4, so that this route to the monoxide involved the difficult preparation of B_2Cl_4. A synthesis of boron monoxide from boron trichloride has now been devised.[44] By reaction with dimethylamine, boron trichloride is converted into chlorobis(dimethylamine)borane (I); which is then reduced by sodium to give a B–B bonded species:

$$\underset{\text{(I)}}{2(Me_2N)_2BCl}+2Na \rightarrow \underset{\text{(II)}}{B_2(NMe_2)_4}+2NaCl$$

The tetrakis(dimethylamino)diboron (II) can be readily hydrolyzed to $B_2(OH)_4$, from which boron monoxide is obtained.

Physical Properties and Structure

The physical properties of gaseous boron monoxide obtained from B–B_2O_3 mixtures have been studied in some detail. In the temperature range 1300–1500°K, mass spectrometric and effusion studies[45] show that a mixture of boron and boric oxide vaporizes very largely as the molecule B_2O_2, with a very low concentration of BO gas. This is confirmed by vapour pressure and molecular weight measurements[46] on the gas in which the presence of BO could not be detected. The vapour pressure of B_2O_2 gas over a B–B_2O_3 mixture varies from $5{\cdot}3\times10^{-8}$ atm at 1300°K to $5{\cdot}3\times10^{-6}$ atm at 1500°K[45]; other workers[46] find vapour pressures 6–8 times larger than these. Thus Scheer[46] found that the vapour pressure of a gas escaping from a B(s)–B_2O_3(l) mixture in the range 1294–1457°K is given by:

$$\log P\,(\text{atm}) = 6{\cdot}609-\frac{72{,}400}{4{\cdot}575T}$$

In order to explain these differences it has been suggested that the equilibration between the condensed phases [B(s), B_2O_3(l) with possibly $(BO)_n$] and B_2O_2 is not readily achieved in the effusion experiments. The heats of vaporization calculated from the vapour-pressure data are probably therefore in considerable error. From the available spectroscopic data however, values of the thermodynamic functions for both (BO)(g) and B_2O_2(g) have been compiled[47] and selected values are given in Tables I and II. The thermodynamic functions for B_2O_2(g) were calculated assum-

Table I.—Thermodynamic Properties of BO(g)

T (°K)	C_p° (cal mole^{-1} deg^{-1})	$H_T^\circ-H_0^\circ$ (kcal mole^{-1})	S_T° (cal mole^{-1} deg^{-1})
298·15	6·978	2·075	48·607
500	7·230	3·504	52·261
1000	8·109	7·355	57·564
1100	8·226	8·172	58·343
1200	8·325	9·000	59·063
1300	8·409	9·836	59·733
1400	8·481	10·681	60·358
1500	8·542	11·532	60·946
1600	8·596	12·389	61·499
1700	8·642	13·251	62·021
1800	8·682	14·117	62·516
1900	8·718	14·987	62·987
2000	8·750	15·861	63·435
2500	8·867	20·267	65·401
3000	8·943	24·721	67·025
4000	9·043	33·718	69·612
5000	9·113	42·798	71·638

Table II.—Thermodynamic Properties of $B_2O_2(g)$

T (°K)	C_p° (cal mole^{-1} deg^{-1})	$H_T^\circ - H_0^\circ$ (kcal mole^{-1})	S_T° (cal mole^{-1} deg^{-1})
298·15	14·418	3·194	59·423
500	16·290	6·313	67·372
1000	18·719	15·148	79·522
1100	18·999	17·034	81·320
1200	19·233	18·946	82·983
1300	19·429	20·880	84·531
1400	19·594	22·831	85·977
1500	19·734	24·798	87·333
1600	19·853	26·777	88·611
1700	19·955	28·768	89·818
1800	20·043	30·768	90·961
1900	20·120	32·776	92·047
2000	20·186	34·792	93·080
2500	20·417	44·948	97·612
3000	20·549	55·192	101·347
4000	20·684	75·818	107·280
5000	20·749	96·538	111·903

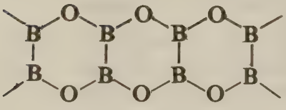
ing a linear O=B—B=O structure and using the fundamental frequencies estimated by Inghram *et al.*[45] The heat and free energy of formation of (BO)(g) have also been compiled[48]; Table III shows representative values. From a study of the MgO–B reaction[32], the heat of formation of B_2O_2(g) at 298°K is found to be -107 ± 4 kcal, in good agreement with other work.[45] From this value, the B–B bond energy in B_2O_2 is estimated[49] to be 120 kcal mole^{-1}. The bond dissociation energies[50] (into gaseous atoms at 0°K) are for BO(g) 189·5 kcal mole^{-1} and for B_2O_2(g), $500{\cdot}5 \pm 10$ kcal mole^{-1}.

Table III.—Heat and Free Energy of Formation of BO(g)

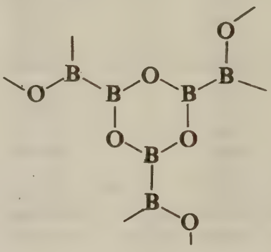
T (°K)	ΔH (kcal mole^{-1})	ΔG° (kcal mole^{-1})
298·16	$-5{\cdot}5$ ($\pm 6{\cdot}0$)	$-12{\cdot}0$ ($\pm 6{\cdot}0$)
500	$-5{\cdot}5$	$-14{\cdot}5$
1000	$-6{\cdot}0$	$-28{\cdot}0$
1100	$-6{\cdot}0$	$-30{\cdot}0$
1200	$-6{\cdot}0$	$-32{\cdot}5$
1300	$-6{\cdot}5$	$-34{\cdot}5$
1400	$-6{\cdot}5$	$-36{\cdot}5$
1500	$-7{\cdot}0$	$-38{\cdot}5$
1600	$-7{\cdot}0$	$-41{\cdot}0$
1800	$-7{\cdot}5$	$-45{\cdot}0$
2000	$-8{\cdot}0$	$-49{\cdot}0$

The infra-red spectrum of B_2O_2(g) has been measured by both emission[50] and absorption.[51–2] Only one band at 1890 cm^{-1} is observed in the emission spectrum; it arises from a B=O stretching mode and is slightly higher than the fundamental of the BO molecule in its ground electronic state. The B_2O_2 molecule is isoelectronic with cyanogen, C_2N_2, and the most likely structure is a linear one ($D_{\infty h}$ symmetry). The infra-red absorption spectrum has similarly been interpreted in terms of the linear structure. The spectra of matrix isolated $^{11}B_2O_2$, $^{11}B^{10}BO_2$ and $^{10}B_2O_2$ show bands only at 1899 cm^{-1}, 1921 cm^{-1} and 1955 cm^{-1}, which are due to the antisymmetric stretching mode in B_2O_2.

The physical properties of the two forms of solid boron monoxide have not been examined in any detail. The high-temperature condensate is a brittle, amber, glassy material amorphous to *X*-rays[35]; the infra-red spectrum[53] shows only very broad bands. It is not soluble in any solvent with which it does not react chemically and the indications are that the high-temperature condensate consists of polymeric BO, $(BO)_n$. The density of $(BO)_n$ determined by flotation[35] is $1{\cdot}765 \pm 0{\cdot}001$ g cm^{-3}. Although the structure of neither solid form has been determined, the chemical evidence indicates them to have a B–B bond for each pair of boron atoms. Possible structures for these polymers include one with linear chains of six-membered B_4O_2 rings (I)[43] (a three-dimensional structure composed of these rings is also possible)[44]; but perhaps the most preferred structure[44] is one built up of six-membered boroxol rings (II).



(I)



(II)

Chemical Properties

The reactions of B_2O_2 gas have not been studied in the absence of a condensed phase. The two solid forms of boron monoxide differ markedly in their chemical properties.

HIGH-TEMPERATURE CONDENSATE

The brown glassy material produced by condensation from high temperatures is more reactive than the white form derived from tetrahydroxydiboron. It is often pyrophoric when exposed to the air for the first time and particularly so when scratched, boric oxide being formed. Samples which are not pyrophoric are otherwise fairly stable to oxidation in dry air; in moist air boric acid is formed slowly.[38] In water, effervescence occurs and hydrogen, containing traces of boranes, is evolved. By using gas chromatography these boranes have been shown to be mainly tetra- and penta-borane in a 5:1 molecular ratio.[54] The resulting aqueous solutions contain some boric acid and show the strong reducing properties of tetrahydroxydiboron, i.e. they decolorize aqueous permanganate and reduce silver salts to the metal.[38] It is apparent, therefore, that when the high-temperature form dissolves, some oxidation of a B–B-bonded species occurs. Under conditions chosen to cause fission of B–B bonds, e.g. when boiled with sodium hydroxide solution in the absence of air, over 90% of the hydrogen according to:

$$2OH^- + B_2O_4^{4-} \rightarrow 2BO_3^{3-} + H_2$$

is evolved.[38]

Alcohols react similarly with $(BO)_n$, the rate of reaction decreasing with increasing molecular weight of the alcohol.[35] With methanol the major reactions occurring are believed to be:

$$B_2O_2 + 4MeOH \rightarrow B_2(OMe)_4 + 2H_2O$$
$$B_2O_2 + 6MeOH \rightarrow 2B(OMe)_3 + 2H_2O + H_2$$

There is no reaction with or solubility in concentrated sulphuric acid, thionyl chloride, acetyl chloride, glacial acetic acid, pyridine, acetone, benzene or diethyl ether.[55]

When heated in vacuo, the amber glassy $(BO)_n$ undergoes blackening at temperatures above 400°C. Differential thermal analysis on a finely ground sample in a nitrogen atmosphere showed[38] an exothermic peak at 439°C, due to the disproportionation:

$$3B_2O_2 \rightarrow 2B + 2B_2O_3$$

Digestion of the product with water enables boric oxide to be leached away and impure boron remains.[37] This disproportionation thus provides a route[38] to elemental boron by carbon reduction of boric oxide (a reaction used industrially for the preparation of boron carbide) according to the scheme:

$$\begin{tikzcd}
C + B_2O_3 \arrow[r, "1100^\circ\text{C}"] & B_2O_2(g) + CO \arrow[d, "\text{Quench to room temperature}"] \\
\frac{n}{3}B + \frac{n}{3}B_2O_3 & (BO)_n \arrow[l, "450^\circ"']
\end{tikzcd}$$

Thermogravimetric analysis[37] of a sample of $(BO)_n$ in air showed no weight change up to 900°C despite disproportionation; the elemental boron is apparently prevented from oxidation by the melt of boric oxide.

Solid $(BO)_n$ does not react when heated with calcium hydride, cobalt(III) fluoride or antimony trifluoride at temperatures up to 600°C, nor with hydrogen chloride at 400°C. When heated in hydrogen, however, above 1100°C, the volatile boroxine is formed.[38] This can be trapped out at −196°C and when warmed to room temperature it evolves diborane:

$$\begin{tikzcd}
3B_2O_2 + 3H_2 \arrow[r, "1100^\circ\text{C}"] & 2B_3O_3H_3(g) \arrow[r, "-196^\circ\text{C}"] & 2B_3O_3H_3(s) \arrow[d, "25^\circ\text{C}"] \\
 & & B_2H_6 + 2B_2O_3
\end{tikzcd}$$

Since the $(BO)_n$ disproportionates before it reaches red heat, this reaction is the hydrogenation of an intimate mixture of boron and boric oxide, which in turn means that it is probably the reaction of hydrogen with gaseous boron monoxide which is evolved[35] by B–B_2O_3 mixtures above 1050°C. Indeed boroxine, $B_3O_3H_3$, and hence diborane, B_2H_6, can be prepared[38] by passing hydrogen over a B_2O_3–C mixture (or any other mixture producing $B_2O_2(g)$[56], e.g. B_4C and TiO_2, B_2O_3 and CaC_2, B_2O_3 and Mg_3B_2) at above 1100°C. This represents an economical route to diborane. If any carbon is present in the reaction mixture, the carbon monoxide formed reacts with the boroxine to form borane carbonyl, which can be decomposed to diborane.

LOW-TEMPERATURE FORM

The boron monoxide formed by dehydration of $B_2(OH)_4$ is a white solid which rapidly absorbs water vapour from the air to reform sub-boric acid. Unlike the high-temperature form, it dissolves in water without evolution of hydrogen and boranes. It is soluble in hot methanol, ethanol, isopropanol and *tert*-butanol without any apparent cleavage of the B–B bond; all the solutions reduce silver nitrate to the metal. It is insoluble in methyl borate (in which boric oxide is soluble) and dimethylamine at the boiling point.

The white boron monoxide remains unchanged when heated to 500°C in vacuo. At 650°C, however, its colour changes to light brown.[43] This brown material resembles the high-temperature form of $(BO)_n$ in being brittle and much less soluble in water and methanol than the original white form; the solution still decolorizes permanganate, however. Samples of white $(BO)_n$ from $B_2(OH)_4$ having the composition $BO{,}0{\cdot}1H_2O$ undergo a rapid and spontaneous change when briefly heated to 400°C, the compound glowing with incandescence. The light brown solid resulting has the same properties as that prepared by heating anhydrous $(BO)_n$.

Refs. p. 222

The most important reactions of the white $(BO)_n$ are those in which it is converted into other B–B bonded species. When it reacts with boron trichloride at 200°C, diboron tetrachloride is formed[44]:

$$\frac{6}{n}(BO)_n + 4BCl_3 \rightarrow 3B_2Cl_4 + 2B_2O_3$$

This reaction provides a particularly useful synthesis since diboron tetrachloride can otherwise only be prepared by electrical discharge methods. Diboron tetrafluoride, which otherwise can only be prepared from diboron tetrachloride, is conveniently made from boron monoxide. The monoxide is allowed to react with sulphur tetrafluoride at −80°C; the mixture is then warmed to room temperature and B_2F_4 obtained[57] by fractionation of the products:

$$2(BO)_n + 2nSF_4 \rightarrow nB_2F_4 + 2nSOF_2$$

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SECTION A6

PROPERTIES AND REACTIONS OF BORIC ACID

BY R. W. SPRAGUE

There are two principal forms of boric acid: orthoboric acid, H_3BO_3, and metaboric acid, HBO_2. Each is a hydrate of boric oxide, B_2O_3, and both are white solids which have moderate solubility in water and dissolve to form the same weakly acid solution. Orthoboric acid is the more stable and the form more commonly encountered, world-wide production now being in excess of 200,000 tons annually. Formerly known also as 'boracic acid', a name which still finds limited use in pharmacy, boric acid and orthoboric acid are synonymous. Metaboric acid, of which there are in fact three crystallographic forms, is much less frequently encountered and when required for chemical reaction it is usually formed by partial dehydration of orthoboric acid *in situ*, as in the largest current use of boric acid, the air oxidation of hydrocarbons. Sub-boric acid, $B_2(OH)_4$, and 'hypoboric' acid, known only as its salts, are not met outside the laboratory; they are reviewed in Sections A8 and B14, respectively.

Preparation and industrial production of the boric acids are described in the following Section (A7). Much of the pure physical chemistry is described here, and some reference is made to aqueous phase systems with inorganic salts. Complexing reactions and complexes formed by interaction between the B—OH groups of the acid and the hydroxyl groups of organic compounds are dealt with in Section A18, where inorganic heteropolyacids containing boron are also described (although these are reviewed more specifically in Section A13). Esters of boric acid are dealt with in Section A17. Boric acid also forms salts with most metals and these salts, the borates, are fully described in Sections A9 and A12. Such salts (and also the heteropolyacids) are almost invariably hydrated when made from boric acid itself; the anhydrous forms are obtained either by subsequent dehydration on heating, often to fusion, or by melting pre-formed boric oxide with metal oxide (or similar).

It is common practice in inorganic boron–oxygen chemistry, in industry and in mineralogy, to employ ratio formulae of a type which indicates the B_2O_3 units. By this mode of formulation, orthoboric acid may be written as $B_2O_3,3H_2O$ and metaboric acid as B_2O_3,H_2O. Similarly, the common form of the principal sodium salt, borax, is frequently referred to as $Na_2O,2B_2O_3,10H_2O$ instead of $Na_2B_4O_7,10H_2O$. This is not meant to imply that B_2O_3 occurs as a B_2O_3 structural unit, but it would be equally erroneous and misleading to infer the presence of a $B_4O_7^{2-}$ anion. Neither should the free acid be regarded as dissociating in solution into BO_3^{3-} anions, but more properly as $B(OH)_4^-$. The actual form which borate ions take in aqueous solution has been the subject of considerable polemic, and is discussed at some length below.

FORMS OF BORIC ACIDS

Discussion of the physical properties and reactions of the boric acids is most appropriately started by consideration of the phase relations in the system boric oxide–water, which establish the solid compounds to be considered. The system has been defined by the classic work of Kracek, Morey and Merwin,[1] who found six stable solid phases in the system, H_2O, H_3BO_3, $HBO_2(I)$, $HBO_2(II)$, $HBO_2(III)$ and B_2O_3, as shown in Fig. 1.

Refs. p. 311. Literature coverage is up to 1974

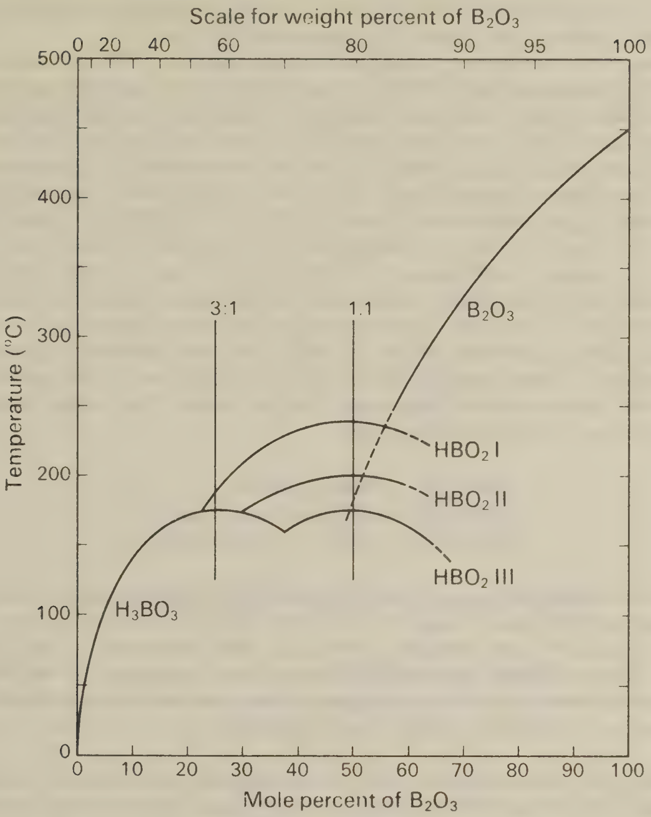


FIG. 1.—Solubility diagram for the system $H_2O–B_2O_3$.[1] (Courtesy of *The American Journal of Science*)

The stability region for ice is tiny and extends only to the cryohydric point (−0·76°C), after which the region for orthoboric acid, H_3BO_3, rises smoothly to a metastable melting point at 170·9°C, then descends to metastable eutectics with HBO_2(II) and finally with HBO_2(III). All three modifications of metaboric acid show relatively flat

Table I.—Invariant Points in the System $B_2O_3–H_2O$[1]

	Wt.-% B_2O_3	Temp., °C
M.p. H_2O	0	0·0
Eutectic—Ice + H_3BO_3	1·28	−0·76
M.p. H_3BO_3	56·3	170·9
$H_3BO_3 \rightleftharpoons HBO_2(I) + $ Liq (incongruent m.p.)	51	169
$H_3BO_3 + HBO_2(II)$, Eutectic	61·6	169·6
$H_3BO_3 + HBO_2(III)$, Eutectic	69·8	158·5
M.p. HBO_2(I)	79·45	236
M.p. HBO_2(II)	79·45	200·9
M.p. HBO_2(III)	79·45	176·0
$HBO_2(III) + B_2O_3$, Eutectic	79·4	176·0
$HBO_2(II) + B_2O_3$, Eutectic	80·6	200·5
$HBO_2(I) + B_2O_3$, Eutectic	82·5	235
M.p. B_2O_3	100·0	450

maxima at the composition corresponding to HBO_2, followed by eutectics with B_2O_3. The invariant points in the system are summarized in Table I.

When boric acid is heated at atmospheric pressure above 100°C, it loses water and is converted into metaboric acid, HBO_2. When the process is carried out below 130°C, the first product is flaky crystals of HBO_2(III). Upon further heating, the HBO_2(III) is converted into coarsely crystalline HBO_2(II). If the temperature is kept below 150°C, the dehydration stops at this point, unless the temperature is maintained for long periods. If the system is heated above 150°C, dehydration continues, yielding a viscous liquid frequently containing some cyrstals of HBO_2(I). If HBO_2(I) crystals are present, they can serve as seed for the crystallization of B_2O_3; neither of the other crystal modifications of metaboric acid seems to be effective for this purpose. If the coarsely crystalline HBO_2(II) is melted in a sealed tube, HBO_2(I) can be slowly crystallized from the melt over a period of weeks. HBO_2(I) is slow to dissolve again, and may be purified by leaching soluble substances off the crystals with water or methyl alcohol.[2]

Other workers[3–7] have made observations on one or more of the isomeric forms of metaboric acid, using various designations for the isomers. Equivalent designations for the various forms of metaboric acid are:

HBO_2(I)—γ-HBO_2 (cubic);
HBO_2(II)—β-HBO_2 (monoclinic);
HBO_2(III)—α-HBO_2 (orthorhombic).

It appears that Stackelberg *et al.*[3] produced HBO_2(II), and reported a melting point of 203°C. Thiel and Siebeneck[4] also worked with HBO_2(II), while Lescoeur[5] prepared HBO_2(III). Tazaki[6–8] first prepared HBO_2(III) and converted it into HBO_2(II) at 160°C; he also concluded[8] that HBO_2(III) can be converted to a 'skeletal' form of boric acid which then converts into the glassy form obtained from HBO_2(II). Methods of preparing and identifying these three crystalline forms have been described by West.[410]

Orthoboric acid and metaboric acid can be regarded as hydrates of boric oxide: $H_3BO_3 = B_2O_3,3H_2O$ and $HBO_2 = B_2O_3,H_2O$. Various workers have considered the possible occurrence of other hydrates of boric oxide and have concluded that there is little evidence to substantiate their existence. Menzel[10, 139, 140] and Banerjee[9, 17] followed the change in X-ray diffraction during the thermal decomposition of orthoboric acid, and found no evidence for other hydrates. Carpeni and Haladjian[11] have claimed the formation of non-stoichiometric phases during the dehydration of orthoboric acid at low (<4 mm Hg) pressures. The formation of these phases is influenced by humidity, heating rate and particle size. There was no evidence for them during dehydration at pressures greater than 4 mm Hg.

Infra-red absorption and X-ray scattering studies of high water-content boric oxide glasses (H_2O/B_2O_3 ratios from 0 to 0·63) indicate that although the network structures of the high-water glasses are somewhat looser than those of low-water glasses, the trigonal coordination of boron, as in boric oxide glass, is maintained.[12–14] Nuclear magnetic resonance studies[15, 16] covering B_2O_3–H_2O compositions from B_2O_3 to $B_2O_3,3H_2O$ confirm the presence of planar triangular BO_3 units over the whole range; however, there was also evidence that the presence of water produced a small percentage of tetrahedral BO_4 units in the wet glasses, as well as in HBO_2(III). Hardness and Young's modulus were not substantially affected by the addition of water.[14]

Forms of boric acid existing in the gas phase have been studied by a number of workers. Stackelberg *et al.*[3] observed the sublimation of orthoboric acid itself and estimated its heat of formation. Others have studied the species formed in the system B_2O_3–H_2O by mass spectrometry[18] and transpiration methods.[19, 28] They concluded that the only species present in significant amounts in the vapour phase are H_3BO_3, HBO_2, $(HBO_2)_3$, B_2O_3 and H_2O. Other H–B–O species are known, but have been shown to contain boron–hydrogen bonds (most commonly they are formed by partial oxidation of boron hydrides); they are discussed elsewhere in connection with boron hydrides (see Part B).

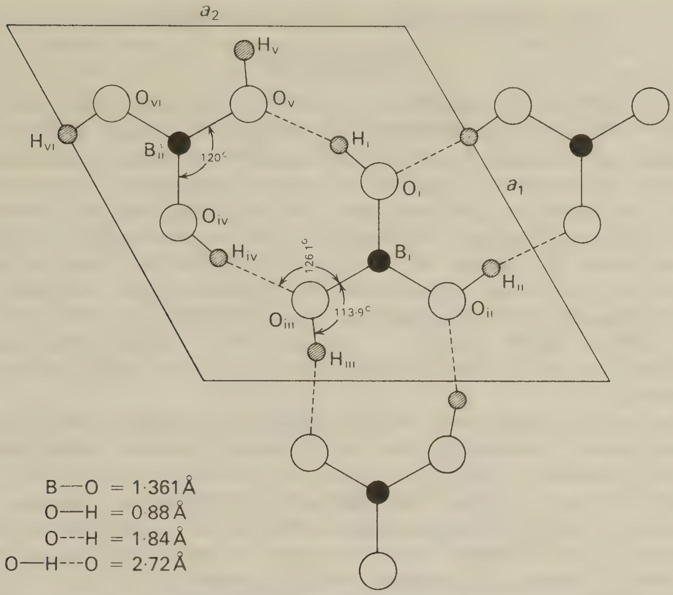


FIG. 2.—The structure of one layer of orthoboric acid[21]

Table II.—Interatomic Distances and Bond Angles in Orthoboric Acid[21]

Distances			
B_i–O_i	1·365 Å	B_{ii}–O_{iv}	1·365 Å
B_i–O_{ii}	1·356 Å	B_{ii}–O_v	1·353 Å
B_i–O_{iii}	1·365 Å	B_{ii}–O_{vi}	1·359 Å
O_i–O_{ii}	2·351 Å	O_{iv}–O_v	2·339 Å
O_{ii}–O_{iii}	2·359 Å	O_v–O_{vi}	2·360 Å
O_{iii}–O_i	2·366 Å	O_{vi}–O_{iv}	2·362 Å
O_i–H_i	0·83 Å	O_{iv}–H_{iv}	0·83 Å
O_{ii}–H_{ii}	0·96 Å	O_v–H_v	0·80 Å
O_{iii}–H_{iii}	0·90 Å	O_{vi}–H_{vi}	0·96 Å
O_i–$H_i \cdots O_v$	2·727 Å	O_{vi}–$H_{iv} \cdots O_{iii}$	2·722 Å
O_{ii}–$H_{ii} \cdots O_{iv}$	2·716 Å	O_v–$H_v \cdots O_v$	2·734 Å
O_{iii}–$H_{iii} \cdots O_{vi}$	2·715 Å	O_{vi}–$H_{vi} \cdots O_i$	2·707 Å
Bond Angles B–O $\wedge$ O–H$\cdots$O			
O_i	112·9°	O_{iv}	114·2°
O_{ii}	116·1°	O_v	113·6°
O_{iii}	113·4°	O_{vi}	113·3°
Mean values			
B–O	1·361 Å	B–O $\wedge$ O–H$\cdots$O	113·9°
O–H$\cdots$O	2·720 Å	B–O $\wedge$ O$\cdots$H–O	126·1°
O–H	0·88 Å		
O$\cdots$H	1·84 Å		

STRUCTURES OF BORIC ACIDS

Orthoboric Acid

The structure of crystalline orthoboric acid has been determined and refined by Zachariasen[20, 21] using X-ray diffraction. It is composed of discrete $B(OH)_3$ molecules, linked together by hydrogen bonds to form infinite layers (not perfectly planar) of nearly hexagonal symmetry. The layers are randomly displaced with respect to each other, giving the crystals triclinic symmetry, and indicating that only Van der Waals forces bind the layers together, which explains the easy cleavage of the crystals into flakes. The structure of a portion of one layer is shown in Fig. 2, and the interatomic distances and angles are summarized in Table II. The triclinic unit cell, space group P_1, contains 4 molecules of $B(OH)_3$, and has the dimensions $a = 7{\cdot}039$, $b = 7{\cdot}053$ and $c = 6{\cdot}578$ Å with $\alpha = 92{\cdot}58°$, $\beta = 101{\cdot}17°$ and $\gamma = 119{\cdot}83°$; layers within the cell are 3·181 Å apart.[21] Tazaki[368] studied twinned crystals of boric acid and laws governing their formation.

In his first paper,[20] Zachariasen did not locate the hydrogen atoms, but he did so in the second paper,[21] establishing their unsymmetrical position. Other workers have used different techniques to study the hydrogen bonds in crystalline boric acid. Electron diffraction[22–4] and the initial interpretation of proton nuclear magnetic resonance spectra[26] indicate that the hydrogen atoms do not lie on a straight line between the oxygen atoms, but are displaced slightly towards the hydrogen atom of the parallel hydrogen bond.[22] However, a neutron diffraction study of $D_3^{11}BO_3$[27] indicates an essentially straight bond in the deuterated acid. Further interpretation and confirmation of the proton nuclear magnetic resonance data show that the results are compatible with a linear O–H–O bond.[25]

Metaboric Acid (III)

The structure of HBO_2(III), the orthorhombic form, has been investigated by X-ray diffraction.[29, 30] The earlier work of Tazaki[29] defined the major features of the structure, which was further refined by Peters and Milberg.[30] It consists of hexagonal $B_2O_3(OH)_3$

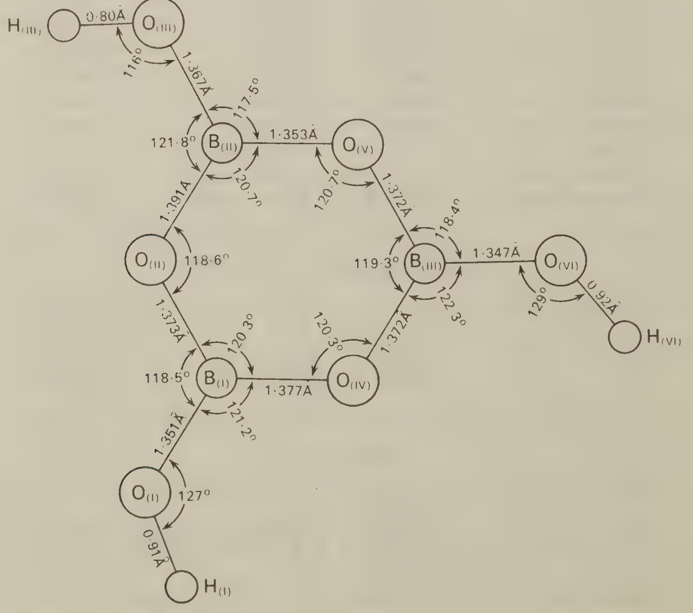


FIG. 3.—Geometry of the $B_2O_3(OH)_3$ molecule in HBO_2(III)[30]

units, linked by hydrogen bonds to form a layered structure; the layers are loosely held together as in orthoboric acid, with a separation of 3·07 Å. The unit cell, orthorhombic, space-group *Pbnm*(D_{2h}^{16}), contains 12 molecules. Unit cell dimensions are (at 25°C) $a=8{\cdot}046$, $b=9{\cdot}688$, $c=6{\cdot}261$ Å. Figure 3[30] illustrates the geometry of the basic $B_3O_3(OH)_3$ molecule, and Fig. 4[30] shows the structure of a portion of one layer of HBO$_2$(III). The average B—O distance in the $B_3O_3(OH)_3$ unit is 1·364 Å, and the average O—H distance is 0·87 Å. There are three distinct O—H···O distances of 2·680, 2·478 and 2·827 Å; bond angles are B–O(H)···O of 120·2°, 119·0° and 114·6°, and B–O···(H)O of 123·7°, 127·0° and 119·9°.

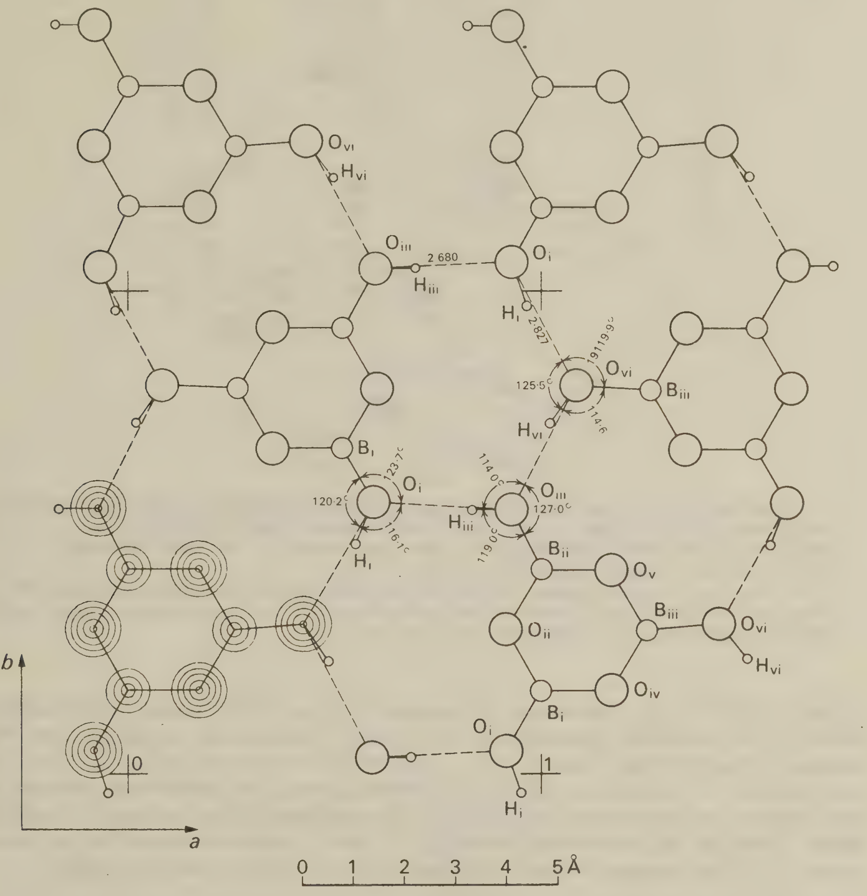


FIG. 4.—Structure of a layer of orthorhombic HBO$_2$. Fourier contours drawn at 2·0 e.Å^{-3} intervals, initial contour: 2·0 e.Å^{-3} [30]

Metaboric Acid (II)

The structure of HBO$_2$(II), the monoclinic form, has been investigated by X-ray diffraction.[31, 33] It is monoclinic, space-group $P2_1/a'$ with 12 molecules per unit cell. Unit cell dimensions are $a=7{\cdot}122$, $b=8{\cdot}842$, $c=6{\cdot}771$ Å, $\beta=93{\cdot}26°$. The structure contains both trigonal and tetrahedral boron atoms, and is the simplest structure with a bond between boron and a water oxygen; i.e. the tetrahedral boron atom is bonded to a water oxygen to form the fourth bond. The structure is illustrated in Fig. 5. The BO$_3$ triangles and BO$_4$ tetrahedra share corners so as to produce endless zigzag chains

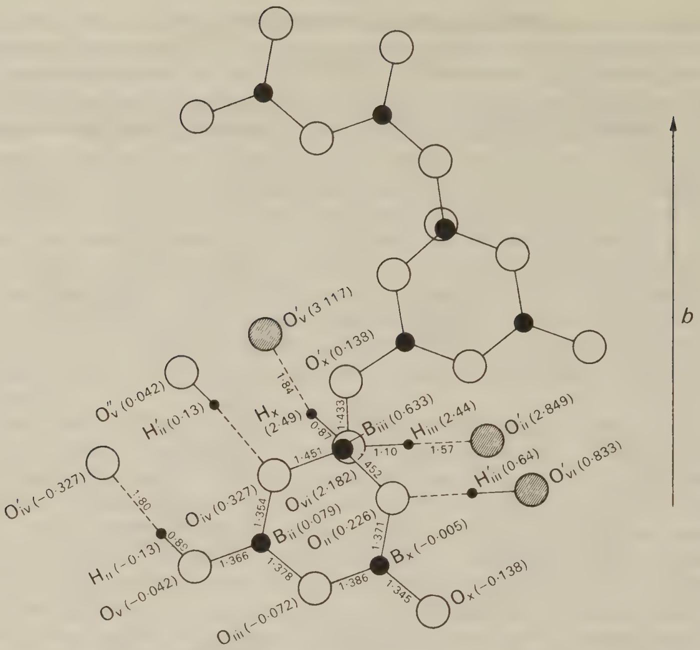


FIG. 5.—Shows a part of the β-HBO_2 structure projected on the (201) plane. The numbers in parentheses give the heights (in Å) of the atoms above or below the plane $2x+z=1$. The lengths of various bonds are indicated in the figure except for the bond of length 1·553 Å between the superimposed atoms B_{iii} and O_{vi}.

The large open circles represent oxygen atoms belonging to the endless chains which are associated with the plane $2x+z=1$, while the shaded large circles denote oxygen atoms belonging to chains of the adjacent plane $2x+z=0$[31]

of $[B_3O_4(OH)(OH_2)]_\infty$. The chains are arranged in layers 3·075 Å apart, with the tetrahedral apices extending alternately up and down. Chains in the same layer are held together by the hydrogen bonds $O_v–H_i \cdots O_{iv}$, while the hydrogen bonds $O_{vi}–H_i \cdots O_v$ and $O_{vi}–H_{iii} \cdots O_{ii}$ link the chains of alternate layers. The interatomic distances in the structure are summarized in Table III. The configuration of oxygen is triangular about B_i and B_{ii}, and tetrahedral about B_{iii}. O_v and O_{vi} are each bonded to two boron atoms. O_{vi} is an oxygen of a water molecule, while O_v is in a hydroxyl group.

Metaboric Acid (I)

The structure of HBO_2(I), the cubic modification, has also been investigated by X-ray diffraction.[33] The crystal is cubic, space-group $P\bar{4}3m$, with 24 molecules per unit cell. The unit cell dimension is $a=8{\cdot}886$ Å. All boron atoms in this structure are tetrahedrally bonded to four oxygens, producing a three-dimensional network of boron tetrahedra. The resulting boron–oxygen configuration is analogous to that found in some forms of silica, but the B–O–B bond angles are smaller than the corresponding Si–O–Si values. The structure of a portion of the network is shown in Fig. 6, and the interatomic distances are summarized in Table IV. The presence of only tetrahedral boron is consistent with the ^{11}B nuclear magnetic resonance data for the crystal, which shows only a single symmetric line.[34]

Thus in metaboric acid there is a gradual transition from all trigonal boron in HBO_2(III), the orthorhombic form, to one-third tetrahedral boron in HBO_2(II), the monoclinic form, and finally all tetrahedral boron in HBO_2(I). This change in structure is consistent with the order of formation during the dehydration of boric acid. That is, the first metaboric acid to form, HBO_2(III), is similar to orthoboric acid itself, with all

Table III.—Interatomic Distances in Monoclinic HBO_2(III)[31]

B_i–O_i	1·345	O_i–O_{ii}	2·335
B_i–O_{ii}	1·371	O_{ii}–O_{iii}	2·392
B_i–O_{iii}	1·386	O_i–O_{iii}	2·380
B_{ii}–O_{iii}	1·378	O_{iii}–O_{iv}	2·378
B_{ii}–O_{iv}	1·354	O_{iii}–O_v	2·350
B_{ii}–O_v	1·366	O_{iv}–O_v	2·368
B_{iii}–$O_{i'}$	1·433	$O_{i'}$–O_{vi}	2·423
B_{iii}–O_{ii}	1·452	$O_{i'}$–O_{ii}	2·449
B_{iii}–O_{iv}	1·451	$O_{i'}$–O_{iv}	2·333
B_{iii}–O_{vi}	1·533	O_{ii}–O_{iv}	2·423
		O_{ii}–O_{vi}	2·386
		O_{iv}–O_{vi}	2·325
H_i–O_{vi}	0·87	O_{vi}–$H_i \cdots O_v$	2·676
H_i–O_v	1·84	O_v–$H_{ii} \cdots O_{iv}$	2·685
H_{ii}–O_v	0·89	O_{vi}–$H_{iii} \cdots O_{ii}$	2·683
H_{ii}–O_{iv}	1·80		
H_{ii}–O_{vi}	1·10		
H_{iii}–O_{ii}	1·57		

Average Distances

B–O	1·367—trigonal	
O–H···O	1·472—tetrahedral	
	2·681	

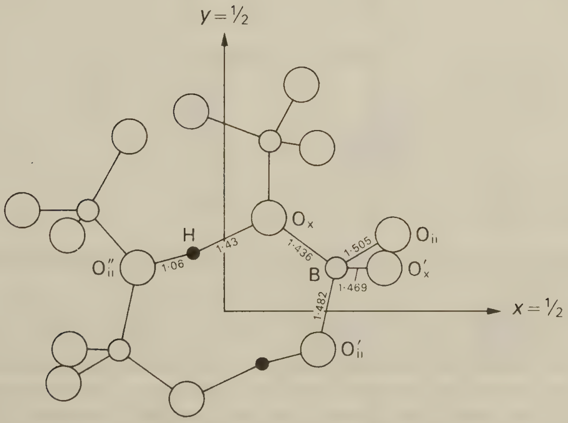


FIG. 6.—Small portions of the three-dimensional tetrahedral network of HBO_2(I) and the hydrogen bonds between tetrahedra. The view is along the Z-axis and the z-coordinates for the labelled atoms are: B (0·3092), H (0·337), O_i (0·3004), O'_i (0·1670), O_{ii} (0·4261), O'_{ii} (0·3551), O''_{ii} (0·3551). The various bond lengths are shown in Å

trigonal boron arranged in pseudo-hexagonal layers and weak Van der Waals bonding between layers. The transition to HBO_2(II) on further heating has been suggested to involve the reaction[35]:

$$n\,B_3O_3(OH)_3 \rightarrow (B_3O_4(OH))_n + nH_2O,$$

with the formed water retained in the structure to form a tetrahedral bond to boron. There are hydrogen bonds between layers, as well as within layers. As a consequence, the crystals of HBO_2(II) are fibrous.[31] The last modification to form, HBO_2(I), contains all tetrahedral boron, as was suggested for crystalline boric oxide,[36] the final stage

Table IV.—Interatomic Distances in Cubic $HBO_2(I)$[33]

$B–O_i$	1·436	$O_i–O'_i$	2·413
$B–O'_i$	1·465	$O_i–O_{ii}$	2·431
$B–O_{ii}$	1·505	$O_i–O'_{ii}$	2·360
$B–O'_{ii}$	1·482	$O_i–O_{ii}$	2·381
		$O'_i–O'_{ii}$	2·421
		$O_{ii}–O'_{ii}$	2·412
$H\cdots O_i$	1·43	$O_i\cdots H–O'_{ii}$	2·487
$H–O''_{ii}$	1·06		

Average

B–O	1·472

Table V.—Mean Bond Lengths (Å) in the Boric Acids[31]

Structure	B–O Boron configuration		$O–H\cdots O$
	Trigonal	Tetrahedral	
H_3BO_3	1·361	—	2·720
$HBO_2(III)$	1·367	—	2·752
$HBO_2(II)$	1·367	1·472	2·681
$HBO_2(I)$	—	1·472	2·486

Interlayer Distances

H_3BO_3	3·181
$HBO_2(III)$	3·128
$HBO_2(II)$	3·075

in the dehydration of orthoboric acid; there is no longer any layer structure, but a three-dimensional network, yielding harder, denser crystals.

The mean bond lengths in the boric acids are summarized in Table V. The mean B—O distances are quite constant, although there are larger deviations for individual bond lengths. The interlayer distances show a steady decrease from orthoboric acid to $HBO_2(II)$, after which the layered structure disappears. The relationships between bond length and bond strength in the boric acids have been discussed by Zachariasen[31] and Coulson.[37]

Although gaseous orthoboric acid exists, direct experimental study of the structure has not been published. Theoretical interpretations of infra-red spectra of the crystalline material have been made, based on a postulated isolated orthoboric acid molecule[38–41]; bond angles and distances were assumed, based on those in the crystal. Calculated

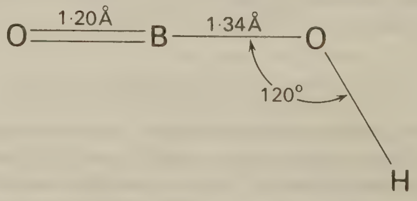


Fig. 7.—Structure of gaseous HBO_2

Table VI.—Infra-red Spectra of Normal and Labelled Orthoboric Acid[47]

Sen[43] H_3BO_3	Matossi and Bluschke[60] H_3BO_3	Duval and Lecompte[44] H_3BO_3	Miller and Wilkins[62] H_3BO_3	Mortimer[61] H_3BO_3	Hornig Plumb[46]	Bethell and Sheppard[51]		Servoss and Clark[47]			Goubeau & Hummel[45]	
						H_3BO_3	D_3BO_3	H_3BO_3	$H_3B^{10}O_3$	D_3BO_3	H_3BO_3	D_3BO_3
								418 (vw)				
										522 (m)	547	513
	532				548	540 (s)		544 (s)	545 (s)	540 (m)	647	637
	633				641	648 (s, b)		639 (s)	629 (sh)	654 (m)		
675								671 (m)	668 (s)	669 (m)		
724	769			703 (vw)			709 (s, b)	690} 800	690} 800		674	
800			807 (m)	799 (m)	750	824 (s, b)		870} (s, b)	870} (s, b)	765 (s, b)		680
							850 (vw, sh)			851 (vw)	798	720
869			885 (vw)	881 (w)	886	882 (vw, sh)		882 (w, sp)	882 (w, sp)		882	831
										878 (vw)		
909							929 (m)			914 (s, sp)		914
990					1110					1045 (m, b)		1030
								1117 (sh)	1117 (sh)			
	1203		1195 (s)	1188 (s)	1196	1197 (s)		1183 (s, sp)	1195 (s, sp)	1181 (m, sh)	1195	
					1220			1220 (sh)	1227 (sh)			
1389		1394										
	1470		1450 (vs)	1457 (vs)?	1493	1450 (s, b)	1420 (s, b)	1428 (vs, b)	1418 (sh)	1428 (vs, b)	1460	1420
								overlapped	1490 (vs)	1470 (sh)		1471
					1670					1690 (vw)		
1818		1815								1830 (vw)		
										1920 (vw)		
				2002 (vw)	1990	2008 (w)		1985 (vw)	1990 (vw)			
				2040 (vw)	2030	2042 (w)		2025 (vw)	2020 (vw)			
				2099 (vw)	2090	2105 (w)		2080 (vw)	2085 (vw)			
				2266 (w)	2255	2280 (m)		2240 (m)	2249 (m)			
					2348		2400 (s, b)	2330 (w)	2340 (w)	2380 (s, sp)		2380
					2490	2505 (m)		2475 (w)	2480 (w)			
				2517 (vw)								
	3060		3270 (s)	3194 (s)	3205	3200 (s, b)		3150 (s, b)	3150 (s, b)	3150 (s, sp)	3210	
				3847 (w)?								

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; vb, very broad; sp, sharp.

results were in good agreement with experiment, and reference is made to some unpublished observations[41] on the gas-phase molecule.

A structure for monomeric, gaseous metaboric acid has been proposed, based on an interpretation of the infra-red emission spectrum[42] of the B_2O_3–H_2O system, and is shown in Fig. 7. It involves a linear O–B–O group with an off-axis hydrogen. The same authors[42] proposed an assumed structure for the gaseous trimer, based on analogy with trimethyl boroxole and borazole; their structure has C_{3h} symmetry with B—O = 1·36, O—H = 1·0 Å and < BOB = 120°.

SPECTRA OF BORIC ACIDS

Infra-red and Raman

Numerous studies of the infra-red absorption and Raman spectra of crystalline boric acids and aqueous solutions of orthoboric acid have been made.[43–66] Results for the infra-red spectra of orthoboric acid reported by various workers are summarized in Table VI. Assignments of the absorptions have been made on the basis of C_{3h} point-group symmetry. Those given by Pistorius[38] are summarized in Table VII, and illustrated in Fig. 8. The shape of the infra-red spectrum depends on both the coordination of boron and the shape of the borate polyion.[480] Results of studies of the Raman spectra are summarized in Table VIII. On the basis of the reported infra-red and Raman spectra, and the assignments made, Pistorius[38] has carried out a normal coordinate treatment by means of Wilson's F–G matrix method.[67, 68] These equations were then used to obtain the most significant valence-type force-constants. Krishnam[69, 70] has conducted a similar treatment, changing two G-matrix elements. These treatments have been questioned by Cyvin *et al.*[39–41], who have carried out a similar treatment themselves, including interaction terms of the G-matrix. The values for in-plane force constants obtained by Cyvin *et al.*[41] are summarized in Table IX.

Table VII.—Fundamental Frequencies of Orthoboric Acid in cm^{-1} [38]

Description	Designation	Symmetry type	$H_3B^{10}O_3$	$H_3B^{11}O_3$	$D_3B^{11}O_3$
O–H stretch	ν_1	*a′*	3250	3250	—
B–O stretch	ν_2		1060	1060	—
BOH bending	ν_3		881	881	—
BO_3 bending	ν_4	*a″*	668	648	541
OH torsion	ν_5		—	824	709
O–H stretch	ν_6	*e′*	3150	3150	2390
B–O stretch	ν_7		1490	1428	1424
OBO bending	ν_8		545	544	504
BOH bending	ν_9		1195	1183	921
OH torsion	ν_{10}	*e″*	—	209(?)	—

The infra-red and Raman spectra of crystalline orthorhombic metaboric acid (HBO_2(III)) has been reported[45, 48]; the results are summarized in Table X. The fundamental vibrations and assignments have been made[48] on the basis of $B_3O_3(OH)_3$ groups with D_{3h} point-group symmetry; assignments for the $B_3O_3(O^-)_3$ skeleton are summarized in Table XI; those for the hydrogen motions (based on D_{2h} point-group symmetry) for the chains of units are summarized in Table XII. Table XIII shows combination and overtone bands in the spectrum. Polycrystalline thin films of orthoboric acid have been studied, at different temperatures and in the presence of different vapours.[396, 397]

The infra-red emission spectrum[42] and absorption spectrum[71] for gaseous metaboric acid have been reported. The absorption measurements are illustrated in Fig. 9, and show no indication of the 1420 cm^{-1} band in the emission spectrum; the emission is postulated to be due to B_2O_3, not HBO_2.[71] The observed frequencies in the emission

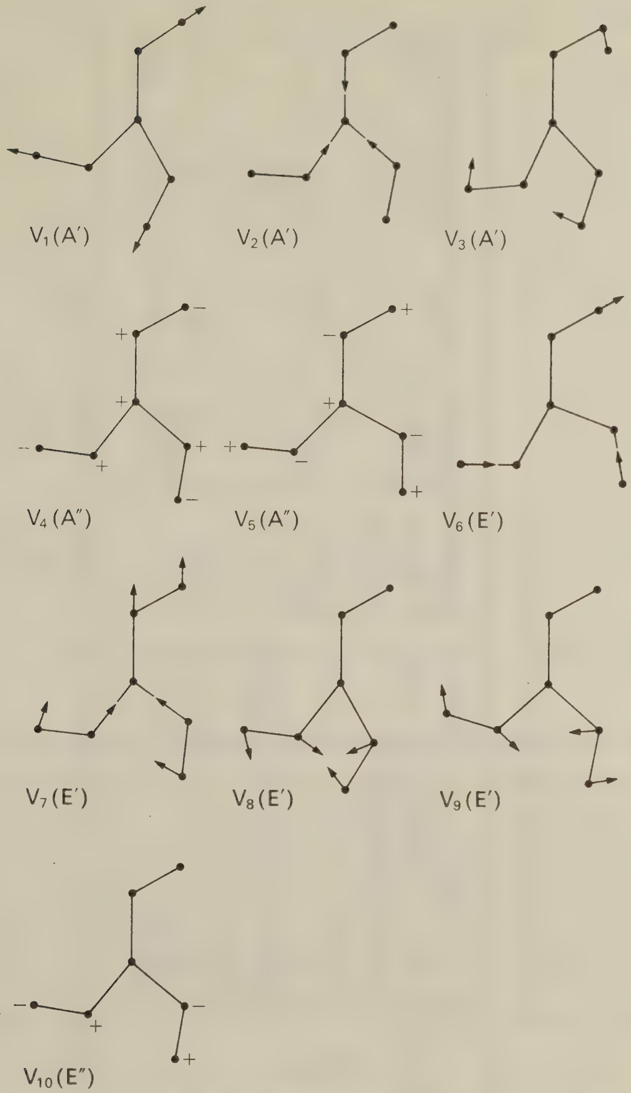


FIG. 8.—Approximate forms of the normal vibrations of the $B(OH)_3$ molecule (point group C_{3h}). Only one of each of the degenerate vibrations is shown. The arrows are not drawn to scale[38]

spectrum are summarized in Table XIV. The absorption spectrum is in agreement (within the experimental error) with the 3680-cm^{-1} and 2030-cm^{-1} frequencies; absorption at wave-lengths longer than 500 cm^{-1} showed no single band, but was attributed to bending motions.[71]

Ultraviolet and Visible Spectra

Studies of ultraviolet and visible absorption spectra of 'boric acids'[72–6] have not clearly established the identity of the species involved. Flame photometric[72–3] and high-temperature[74, 75] work may involve metaboric acid species, but may equally well involve species containing only boron and oxygen.

Table VIII.—Raman Spectrum of Orthoboric Acid

Ananthakrishnan[52, 63]		Mitra[58]		Hibben[65]		Kahovec[59]	Kujumzelis[66]	Mitra[69]	Servoss and Clark[47]	Goubeau & Hummel[45]	
Cryst.	Aq. sol.	Conc. sol.	Dil. sol.	Cryst.	Aq. sol.	Cryst.	Aq. sol.	Cryst.		H_3BO_3	D_3BO_3
		515		503 (4)	506 (2) (bd)		(400–500)		500 (2)	500	
			710								675
	875 (5)	872	872	880 (6)	873 (6)	883 (5)	878 (st)	882	830 (5)	715	
			909							798	831
		986								880	
				1065 (0)	1060 (0)	1032 (vw)				1067	
					1130 (0)	1169 (vw)				1155	
				1155 (0)							
		1340			1420 (1) (bd)	1391 (vw)	(1400)		1430 (1)	1505	1458
3172				3180 (3)		3170 (3b)		3195			
3256				3256 (2)		3248 (2b)		3290	3200 (vb, s)	3173	2405
				3574 (3)						3250	2500

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; vb, very broad; sp, sharp.

Table IX.—In-plane Valence Force-constants (f in mdyne/Å) and Compliance Constants (n in Å/mdyne) for Orthoboric Acid[41]

	$x=d$	$x=r$	$x=\alpha$	$x=\beta$		
f_x	5·697	6·788		0·426		
f_{dx}	0·097	−0·016		−0·006		
f'_{dx}		0·027	$f_{d\alpha}$+0·025	0·008		
f''_{dx}		−0·011	$f_{d\alpha}$+0·016	0·001	$f_{\beta\beta}$	−0·054
	$x=r$	$x=\alpha$	$x=\beta$		$x=\alpha$	$x=\beta$
f_{rx}	1·321		0·007	$f_{\alpha x}$	f_{α}−1·170	
f'_{rx}		$f_{r\alpha}$+0·393	−0·051	$f'_{\alpha x}$		$f_{\alpha\beta}$−0·442
f''_{rx}			0·118	$f''_{\alpha x}$		$f_{\alpha\beta}$+0·040
	$x=d$	$x=r$	$x=\alpha$	$x=\beta$		
n_x	0·176	0·160	0·937	3·300		
n_{dx}	−0·003	0·001	0·002	0·001		
n'_{dx}		−0·001	−0·001	−0·001		
n''_{dx}		0·000	−0·001	−0·001	$n_{\beta\beta}$	−0·072
	$x=r$	$x=\alpha$	$x=\beta$		$x=\alpha$	$x=\beta$
n_{rx}	−0·027	0·044	−0·020	$n_{\alpha x}$	−0·469	−0·390
n'_{rx}		−0·022	−0·002	$n'_{\alpha x}$		0·889
n''_{rx}			−0·002	$n''_{\alpha x}$		−0·498

Nuclear Magnetic Resonance and Electron-spin Resonance Spectra

The proton nuclear magnetic resonance spectrum in crystalline orthoboric acid has been investigated in connection with studies of the hydrogen bond.[26, 77, 78] The ^{11}B nuclear magnetic resonance spectrum in orthoboric acid, monoclinic and orthorhombic metaboric acid (HBO_2(II) and (III))[16], and in cubic metaboric acid (HBO_2(I))[79] have all been determined. The quadrupole coupling constants vary from near zero (0·85) for the tetrahedral boron in cubic metaboric acid to 2·56 for trigonal boron in orthoboric acid. The ^{11}B nuclear magnetic resonance of aqueous boric acid solutions was found to be a single line, independent of concentration.[80] The pH dependence of the ^{11}B shift in boric acid–borate solutions has been studied.[398, 479] The electron spin resonance spectra of irradiated orthoboric acid and deutero-orthoboric acid have been studied.[81]

PHYSICAL PROPERTIES OF THE BORIC ACIDS

The specific gravity of crystalline orthoboric acid at several temperatures has been summarized in Mellor.[82] The thermal expansion in the temperature range 30°–80°C was determined by an X-ray method[83]; the three-directional expansion coefficients are $a_{11}=3{\cdot}67\pm0{\cdot}6\times10^{-6}$, $a_{22}=10{\cdot}83\pm1{\cdot}0\times10^{-6}$ and $a_{33}=255{\cdot}9\pm1{\cdot}0\times10^{-6}$; the direction of maximum expansion is nearly perpendicular to the plane of the oxygen atoms, while the direction of negative expansion is parallel to the shortest hydrogen bonds. Tazaki[8] determined the changes in density and weight loss caused by heating orthoboric acid to temperatures ranging from 40° to 200°C. He concluded that the densities of the boric acids are as follows (g cm^{-3}): orthoboric acid 1·504; HBO_2(III) 1·78; HBO_2(II) 2·04; and HBO_2(I) 2·49, again presumably at ambient temperature. Sokolova and Skuratov[155] report HBO_2(III) $1{\cdot}786\pm0{\cdot}004$ and HBO_2(II) $2{\cdot}040\pm0{\cdot}004$ at 25°C. Kracek *et al.*[1] report 1·78 for HBO_2(III), 2·044 for HBO_2(II) and 2·485 for HBO_2(I).

Table X.—Infra-red and Raman Spectra (cm^{-1}) *of Orthorhombic Metaboric Acid*[48]

Goubeau and Hummel[45] [a]		Parsons[48]			Raman $B_3O_3(OH)_3$
$B_3O_3(OH)_3$	$B_3O_3(OD)_3$	$B_3O_3(OH)_3$	$B_3{}^{10}O_3(OH)_3$	$B_3O_3(OD)_3$	
262 (vw)					
268 (vw)					
274 (vw)					
280 (m)					
415 (m)					
456 (s)					
462 (m, sh)		462 (m)	463 (m)	456 (m)	
476 (m)		478 (w, sh)	482 (w, sh)	474 (w, sh)	
		504 (vw)	504 (vw)	499 (m)	
		548 (vw)		577 (w)	
591 (m)		595 (w)	600 (w)	600 (s, b)	598 ± 3 (s)
645 (s)		650 (w)	650 (vw)	639 (w)	
			675 (w)	680 (w)	
	718 (s, b)			727 (m)	
735 (s, b)		745 (s, b)	761 (s, b)	739 (s, b)	
				805 (vw)	
825 (s, b)	835 (w)	833 (s, b)	835 (s, b)	842 (m)	819 ± 5 (s)
				865 (vw)	
885 (vw)	880 (w)			887 (m)	
942 (m)	925 (w)	939 (m)	942 (m)	930 (m)	
960 (vw)	970 (vw)	956 (w)	960 (w)	972 (w)	
	1005 (m)			1004 (s)	
1110 (w)		1099 (m)	1099 (m)		
		1132 (m)			
1150 (m)	1160 (w, b, sh)	1147 (s)	1153 (s)	1126 (w)[a]	
1200 (s)		1196 (m)	1212 (s)		
1245 (w)		1239 (s)	1267 (m)	1226 (w)	
1290 (w, sh)		1289 (w)	1300 (m)		
		1342 (vs)			
1375 (vs, vb)	1350 (vs, vb)	1360 (vs)		1358 (vs, b)	
		1397 (vs, vb)	1385 (vs, vb)	1407 (vs, b)	
1450 (s, vb)			1451 (vs, vb)	1441 (m, b)	
	1475 (w, sh)	1473 (m)		1477 (m, b)	
			1523 (m)	1504 (m, b)	
		1754 (vw)	1754 (vw)	1775 (vw)	
				1812 (vw)	
		1905 (vw)	1892 (vw)		
		1942 (vw)	1976 (vw)	1930 (vw)	
		2041 (vw)	2041 (vw)	2008 (vw)	
		2088 (vw)	2088 (vw)		
		2151 (vw)			
		2188 (vw)	2179 (vw)	2193 (vw)	
		2227 (vw)	2227 (vw)	2227 (vw)	
		2294 (vw)			
		2342 (vw)	2353 (vw)	2398 (s)	
		2415 (vw)	2410 (vw)	2454 (s)	
		2475 (vw)	2485 (vw)	2506 (s)	
		2646 (vw)	2717 (vw)	2825 (vw)	
		3195 (s)	3195 (s)		
		3257 (s)	3257 (s)	3215 (w)[a]	
		3356 (s)	3356 (s)		

[a] Absorption resulting from residual OH groups.

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; vb, very broad; sh, shoulder; sp, sharp.

Table XI.—Selection Rules, Description of Normal Vibrations and Frequency (cm^{-1}) *Assignments for the* $B_3O_3(O^-)_3$ *Skeleton of Orthorhombic Metaboric Acid for Point Group* D_{3h}

Species and activity	Description of normal vibration	Assignment[a]	Infra-red			Raman
			$B_3O_3(OH)_3$	$B_3{}^{10}O_3(OH)_3$	$B_3O_3(OD)_3$	$B_3O_3(OH)_3$
d_1' Raman	[b]Symmteric B–OH[c] stretching	ν_1	1239	1267	1226	
	[b]Trigonal deformation of the B_3O_3 ring	ν_2	[d]	[d]	805	819
	[b]Ring breathing (B–OH groups in phase)	ν_3	595	600	577	598
d_2' Inactive	[b]B atoms twisting against the O atoms	ν_4	1473	1523	1441	
	[b]OH groups twisting against the ring	ν_5	478	482	474	
E' Infra-red Raman	B–OH stretching	ν_6	1397	1451	1407	
	Ring stretching	ν_7	$\begin{cases}1342\\1360\end{cases}$	1385	1358	
	Ring stretching	ν_8	939	942	930	
	Ring angle bending	ν_9	462	463	456	
	B–OH rocking	ν_{10}	280[e]			
d_2'' Infra-red	Out-of-plane ring mode (B and O atoms out of phase)	ν_{11}	745	761	$\begin{cases}727\\739\end{cases}$	
	B–OH wagging (OH groups in phase)	ν_{12}	(200)[f]			
E'' Raman	[b]B–OH wagging	ν_{13}	650	675	639	
	Out-of-plane ring mode	ν_{14}	(215)[f]			

[a] Numbering follows the Herzberg scheme.
[b] Vibrations active under the site group symmetry C_{2v}.
[c] Oxygen atoms not in ring distinguished as OH groups.
[d] Obscured by strong OH absrоption.
[e] From footnote reference 45.
[f] Estimated from data in Nielsen, J. R., Liang, C. & Smith, D. C., *Discussion Faraday Soc.*, 1950, **9**, 177.

Table XII.—Selection Rules, Description of Hydrogen Motions and Frequency (cm^{-1}) Assignments for the Hydrogen–Oxygen Chain for the Factor Group Isomorphic with the Point Group D_{2h}[48]

Species and activity	Description of hydrogen motion	Assignment	Infra-red		
			$B_3O_3(OH)_3$	$B_3{}^{10}O_3(OH)_3$	$B_3O_3(OD)_3$
A_g Raman	Stretching In-plane bending	ν_1^H ν_2^H			
B_{1g} Raman	Stretching In-plane bending (R_z)	ν_3^H ν_4^H			
B_{2g} Raman	Out-of-plane bending (R_y)	ν_5^H			
B_{3g} Raman	Rotation about the chain axis (R_x)	0			
A_u Inactive	Out-of-plane bending Out-of-plane bending	ν_6^H ν_7^H			
B_{1u} Infra-red	Out-of-plane bending Translation (T_z)	ν_8^H 0	833	835	600
B_{2u} Infra-red	Stretching In-plane bending In-plane bending Translation (T_y)	ν_9^H ν_{10}^H ν_{11}^H 0	3356 1196 1147	3356 1212 1153	2506 1004 887
B_{3u} Infra-red	Stretching Stretching In-plane bending Translation (T_x)	ν_{12}^H ν_{13}^H ν_{14}^H 0	3257 3185 1099	3257 3195 1099	2454 2398 842

Table XIII.—Interpretation of Combination and Overtone Bands in the Infra-red Spectrum of Orthorhombic Metaboric Acid, $B_3O_3(OH)_3$[48]

Observed frequency in cm^{-1}	Interpretation
415	(200)+(215)=415 (E')
548	2×280=560 ($A_1'+A_2'+E'$)
956	(215)+745=960 (E')
1132	?
1289	?
1754	?
1905	?
1942	595+1360=1955 (E')
2041	939+1099=2038
2088	939+1147=2086
2151	939+1196=2135
2188	819+1360=2179 (E') 939+1239=2178 (E')
2227	819+1397=2216 (E')
2294	939+1360=2299 ($A_1'+A_2'+E'$)
2342	939+1397=2336 ($A_1'+A_2'+E'$)
2415	939+1473=2412 (E')
2475	?
2646	1239+1397=2636 (E')

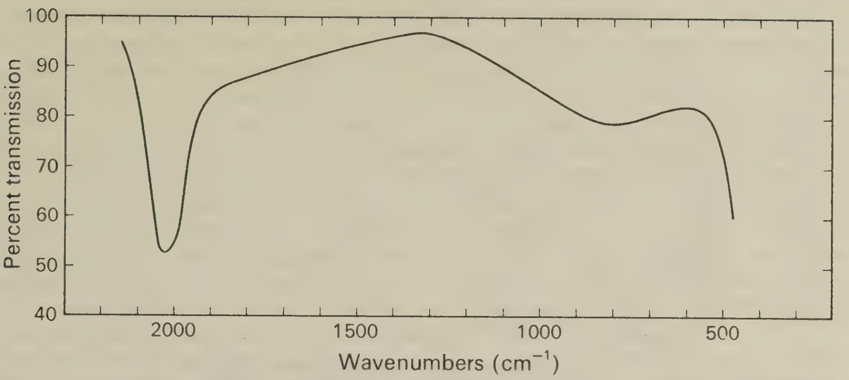


FIG. 9.—Absorption spectrum of HBO_2 formed by heating B_2O_3 to 1160°C in presence of 2 cm Hg pressure of water vapour. Spectrum plotted point by point using power-on/power-off technique. Path length 120 ft, NaCl prism[71]

Table XIV.—Frequency Assignment for Gaseous HBO_2 [71]

Species	Frequency (cm^{-1})[a]	Approx. character of mode
A′	3680	O—H stretch
	2030	B═O stretch
	1420	B—O stretch
	(1250)	O—H bend
	(600)	O—B═O bend
A″	(700)	O—B═O bend

[a] The frequencies given in parentheses have been estimated. The others have been observed in natural HBO_2(g).

The elastic and torsion moduli, double refraction, dispersion, elliptical polarization, index of refraction, molecular refraction and magnetic susceptibility for orthoboric acid have been discussed in Mellor.[82] The magnetic susceptibility recorded there is $-0{\cdot}6 \times 10^{-6}$; more recent values are $-34{\cdot}8 \times 10^{-6}$ [163] and $-35{\cdot}72 \times 10^{-6}$ [164] c.g.s. units. The crystals have a dark conductive resistance of $(1 \text{ to } 3) \times 10^{15}$ ohm[165], and were reported to show no photoconductivity. However, others[87] dispute this, asserting that light at 2537 Å produces photoconductivity. Kracek *et al.*[1] provide data on refractive indices of orthoboric acid as α 1·337, β 1·461 and γ 1·462; for the metaboric acids they report HBO_2(III), α 1·376, β1·514, γ 1·619. The data of Batsanov[371] for orthoboric acid at several wave-lengths are summarized in Table XIVa.

Table XIVa.—Refraction of Orthoboric Acid

λ (nm)	n_γ	n_β	n_α
486	1·468	1·466	1·340
520	1·4655	1·4635	—
555	1·4635	1·4615	—
589	1·462	1·460	1·338
656	1·461	1·459	1·337
∞	1·452	1·450	1·333

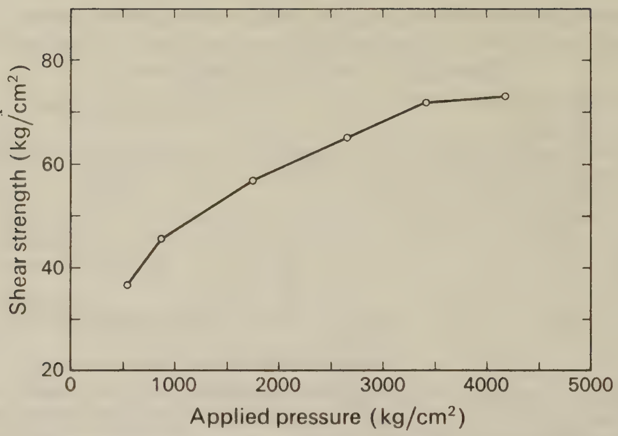
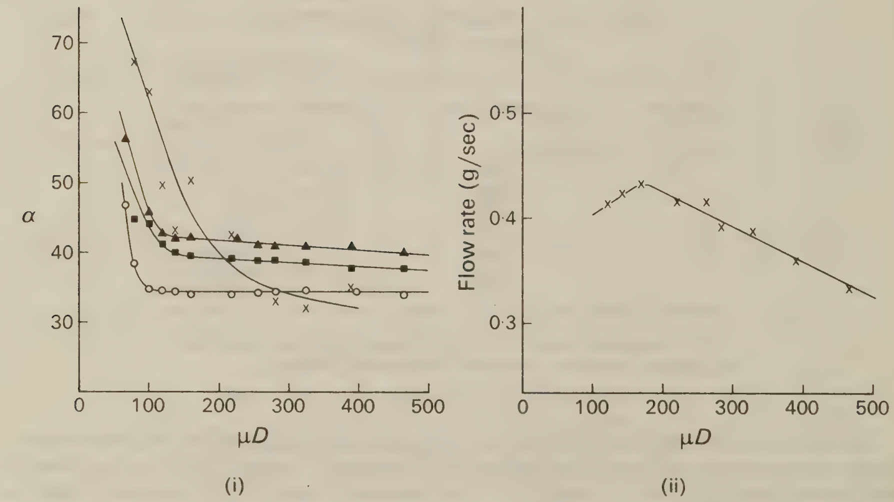


FIG. 9a.—Effect of applied pressure on shear strength of boric acid powder[374]



(i)
(ii)

FIG. 9b.[375]

(i) Dependence of particle size on angle of repose or sliding angle of boric acid powders.
(ii) Effect of particle size on flowing rate.
x Boric acid powders

The volume compression of orthoboric acid to a maximum pressure of 10,000 atmospheres has been determined[84] to fit the equation

$$-\Delta V/V = (11{\cdot}65\times10^{-6})(P-2000)-(1{\cdot}11\times10^{-10})(P-2000)^2(P \text{ in atm.}).$$

The effect of applied pressure on the shear strength of compacted orthoboric acid powder is illustrated in Fig. 9a.[374] Kaneniwa *et al.*[375] have studied the relationship between particle size and angle of repose or sliding angle for orthoboric acid powders. Their results are illustrated in Fig. 9b, which also shows the flow rate of orthoboric acid powders as a function of particle size.

The dielectric constant of pressed boric acid powder was found to remain constant from −120° to 40°C, then rise to a maximum near 100°C, fall to a minimum near 150°C, and finally rise to a constant level at about 200°C. The dichroism produced by ultrasound in suspensions of boric acid crystals in organic media has been studied.[86]

Thermodynamic data pertinent to the boric acids have been reviewed in the JANAF Tables[89], and selected values have been used to calculate thermodynamic functions at even 100 K intervals from 0 to 6000 K. The heat of formation of crystalline orthoboric acid selected is −261·47 kcal/mol at 25°C.[393] The heat of formation of gaseous orthoboric acid is calculated from that of the crystal and the heat of sublimation (24·3 kcal/mol) derived from vapour-pressure data.[3] The heat of formation of HBO_2(I) (−191·87 kcal/mol) was taken from Kilday and Prosen's[2] heat of hydrolysis measurements and the above heat of formation of orthoboric acid. West determined the heats of formation of the three forms of metaboric acid relative to orthoboric.[410] The heat of formation of monomeric gaseous metaboric acid (−134·0 kcal/mol) was taken from the average of four studies of the heat of hydrolysis of molten boric oxide[18] and data for water and boric oxide.[395] The heat of sublimation of H_3BO_3 at 298·1 K has been determined as 18·05 kcal/mol and entropy as 60·6 cal/mol degree.[417]

The low-temperature heat capacity of orthoboric acid has been determined in the temperature range 16–296 K[88]; these data, plus estimates based on values for the constituent oxides, were used to prepare tables of values at 100 K intervals[89] from 0 to 1500 K; the value at 25°C is 19·44 cal/mol°C. The fundamental frequencies obtained by Pistorius[38] were used to calculate heat capacities of gaseous orthoboric acid by methods of statistical thermodynamics,[89] and to prepare tables at 100 K intervals from 0–6000 K; the value at 25°C for gaseous H_3BO_3 is 15·616 cal/mol°C.

Heat capacities for crystalline cubic metaboric acid (HBO_2(I)) have been estimated from values for the constituent oxides, and used to prepare tables at 100 K intervals; the value at 25°C is 13 cal/mol°C.[89] The data for the fundamental frequencies of gaseous metaboric acid from the work of White *et al.*[42] were used to calculate heat capacities for gaseous HBO_2 for the temperature interval 0–6000 K[89]; the value at 35°C is 10·094 cal/mol°C. The calculated thermodynamic functions derived from the above data are shown in Tables XIVb–XIVf.

Table XIVb.—Thermodynamic Functions for Boric Acid (H_3BO_3) (Crystal) mol wt = 61·844[89]

	cal/(mol deg)			kcal/mol			
T, K	C_p°	S°	$\frac{-(F^\circ-H^\circ_{298})}{T}$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	0·000	0·000	Infinite	−3·201	−258·231	−258·231	Infinite
100	8·585	6·927	34·737	−2·781	−260·025	−250·823	548·146
200	14·040	14·610	22·315	−1·641	−260·889	−241·267	263·632
298	19·440	21·210	21·210	0·000	−261·470	−231·503	169·688
300	19·540	21·331	21·210	0·036	−261·478	−231·317	168·507
400	23·950	27·579	22·633	2·219	−261·725	−221·218	120·862
500	27·400	33·302	23·723	4·790	−261·712	−211·088	92·262
600	30·400	38·569	25·764	7·683	−261·476	−200·982	73·204
700	32·963	43·452	27·946	10·854	−261·041	−190·930	59·608
800	35·200	48·003	30·172	14·265	−260·431	−180·957	49·433
900	37·050	52·258	32·392	17·879	−259·672	−171·066	41·539
1000	38·700	56·249	34·581	21·668	−258·785	−161·266	35·243
1100	40·147	60·007	36·723	25·612	−257·793	−151·563	30·111
1200	41·400	63·555	38·813	29·691	−256·706	−141·951	25·852
1300	42·460	66·912	40·845	33·886	−255·547	−132·436	22·263
1400	43·327	70·092	42·823	38·177	−254·330	−123·011	19·202
1500	44·000	73·105	44·742	42·545	−253·078	−113·674	16·562

Table XIVc.—Thermodynamic Functions for Boric Acid (H_3BO_3)
(*Ideal Gas*) *mol wt* = *61·844*[89]

	cal/(mol deg)			kcal/mol			
T, K	C_p°	S°	$\frac{-(F^\circ - H_{298}^\circ)}{T}$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_P
0							
100	11·043	56·791	82·550	−2·576	−235·509	−231·294	505·469
200	12·873	64·896	71·877	−1·396	−236·334	−226·770	247·791
298	15·616	70·539	70·539	0·000	−237·160	−221·900	162·649
300	15·669	70·636	70·539	0·029	−237·175	−221·806	161·578
400	18·371	75·522	71·187	1·734	−237·900	−216·570	118·323
500	20·640	79·874	72·497	3·688	−238·503	−211·166	92·296
600	22·471	83·805	74·059	5·847	−239·002	−205·650	74·904
700	23·966	87·384	75·711	8·171	−239·414	−200·055	62·457
800	25·215	90·668	77·378	10·632	−239·754	−194·411	53·108
900	26·280	93·701	79·026	13·208	−240·033	−188·726	45·827
1000	27·199	96·519	60·636	15·883	−240·260	−183·011	39·995
1100	27·997	99·150	82·201	18·644	−240·451	−177·279	35·220
1200	28·693	101·616	83·717	21·479	−240·608	−171·526	31·236
1300	29·300	103·937	85·184	24·380	−240·743	−165·765	27·866
1400	29·832	106·129	86·602	27·337	−240·860	−159·993	24·975
1500	30·298	105·203	87·974	30·344	−240·969	−154·212	22·468
1600	30·708	110·172	89·300	33·395	−241·074	−148·427	20·273
1700	31·069	112·045	90·584	36·484	−241·173	−142·631	18·336
1800	31·387	113·830	91·826	39·607	−241·274	−136·834	16·613
1900	31·669	115·534	93·029	42·760	−241·375	−131·026	15·071
2000	31·920	117·165	94·195	45·940	−241·477	−125·217	13·682
2100	32·143	118·728	95·327	49·143	−241·582	−119·400	12·426
2200	32·343	120·228	96·425	52·368	−241·694	−113·580	11·283
2300	32·522	121·670	97·491	55·611	−241·808	−107·756	10·239
2400	32·683	123·058	98·528	58·871	−241·931	−101·921	9·281
2500	32·827	124·395	99·536	62·147	−247·451	−95·982	8·390
2600	32·958	125·685	100·517	65·436	−247·580	−89·917	7·558
2700	33·077	126·931	101·472	68·738	−247·715	−83·850	6·787
2800	33·185	128·136	102·403	72·051	−247·856	−77·761	6·071
2900	33·283	129·302	103·311	75·375	−248·002	−71·696	5·403
3000	33·373	130·432	104·196	78·708	−248·154	−65·619	4·780
3100	33·455	131·528	105·060	82·049	−248·310	−59·534	4·197
3200	33·530	132·591	105·904	85·398	−248·475	−53·441	3·650
3300	33·599	133·624	106·728	88·755	−248·646	−47·343	3·135
3400	33·663	134·628	107·534	92·118	−248·824	−41·242	2·651
3500	33·721	135·604	108·322	95·487	−249·009	−35·133	2·194
3600	33·776	136·555	109·093	98·862	249·201	−29·018	1·762
3700	33·826	137·481	109·848	102·242	−249·402	−22·897	1·352
3800	33·873	138·384	110·587	105·627	−249·608	−16·770	0·964
3900	33·916	139·264	111·311	109·017	−249·822	−10·645	0·596
4000	33·957	140·124	112·021	112·410	−371·224	−2·368	0·129
4100	33·994	140·963	112·717	115·808	−371·221	6·854	−0·365
4200	34·029	141·782	113·399	119·209	−371·225	16·082	−0·837
4300	34·062	142·583	114·068	122·614	−371·237	25·305	−1·286
4400	34·093	143·367	114·725	126·022	−371·257	34·519	−1·715
4500	34·122	144·133	115·370	129·432	−371·285	43·741	−2·124
4600	34·149	144·883	116·004	132·846	−371·318	52·975	−2·517
4700	34·175	145·618	116·626	136·262	−371·360	62·198	−2·892
4800	34·199	146·338	117·238	139·681	−371·408	71·424	−3·252
4900	34·221	147·043	117·839	143·102	−371·463	80·643	−3·597
5000	34·242	147·735	118·430	146·525	−371·524	89·866	−3·928
5100	34·263	148·413	119·011	149·950	−371·595	99·104	−4·247
5200	34·282	149·079	119·583	153·377	−371·670	108·324	−4·553
5300	34·300	149·732	120·146	156·807	−371·751	117·566	−4·848
5400	34·317	150·373	120·700	160·237	−371·842	126·788	−5·131
5500	34·333	151·003	121·245	163·670	−371·936	136·033	−5·405
5600	34·348	151·622	121·782	167·104	−372·040	145·257	−5·669
5700	34·363	152·230	122·311	170·539	−372·150	154·499	−5·924
5800	34·376	152·828	122·832	173·976	−372·266	163·741	−6·170
5900	34·390	153·415	123·345	177·415	−372·388	172·987	−6·408
6000	34·402	153·993	123·851	180·854	−372·517	182·234	−6·638

Mar. 31, 1961; Dec. 31, 1964

Table XIVd.—Thermodynamic Functions for Metaboric Acid (HBO_3) (Crystal) mol wt = 43·828[89]

	cal/(mol deg)			kcal/mol			
T, K	C_p°	S°	$\frac{-(F^\circ - H_{298}^\circ)}{T}$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_P
0							
100							
200							
298	13·000	11·700	11·700	0·000	−191·870	−175·677	128·769
300	13·100	11·781	11·700	0·024	−191·870	−175·577	127·902
400	14·700	15·778	12·234	1·417	−191·857	−170·147	92·959
500	15·900	19·187	13·292	2·947	−191·821	−164·723	71·997
600	17·100	22·188	14·529	4·595	−191·753	−159·309	58·025
700	18·863	24·961	15·823	6·396	−191·597	−153·912	48·051
800	20·300	27·577	17·131	8·357	−191·332	−148·547	40·579
900	21·425	30·036	18·429	10·446	−190·979	−143·219	34·777
1000	22·200	32·337	19·706	12·630	−190·566	−137·933	30·144
1100	22·480	34·466	20·953	14·865	−190·137	−132·691	26·362
1200	22·700	36·432	22·162	17·124	−189·712	−127·486	23·217
1300	22·860	38·256	23·331	19·403	−189·296	−122·319	20·563
1400	22·960	39·954	24·458	21·694	−188·893	−117·181	18·292
1500	23·000	41·540	25·545	23·993	−188·509	−112·074	16·328

Vapour Pressure of Boric Acids

The volatility, or 'steam volatility', of the boric acids has been a subject of controversy for many years. The questions whether they are volatile, what species vaporize, and what species exist in the gas phase, and factors affecting the vaporization equilibrium and vaporization rates, are still not completely resolved. It appears that much of the argument is derived from the possibility for dehydration (or hydration) according to the equations:

$$H_3BO_3(s \text{ or } g) \rightleftharpoons HBO_2(s) + H_2O(g)$$
$$HBO_2(s) \rightleftharpoons B_2O_3(s) + H_2O(g)$$

There appears to be general agreement at this time that, other than $H_2O(g)$, $H_3BO_3(g)$ is the predominant, if not the only, gaseous species at relatively low temperatures ($<160°C$).[3] As the temperature is increased $HBO_2(g)$ becomes significant, and at still higher temperatures $(HBO_2)_3(g)$ becomes significant.[18, 19, 42] The total pressure observed, therefore, depends upon the overall composition of the total system, and whether any condensation of HBO_2 has occurred in cooler portions of the system. Most of the observed total pressure is, of course, due to $H_2O(g)$ from the dehydration equilibria. That is, starting with pure boric acid, as the temperature is raised (in a closed system) eventually the melting point is reached, following which the vapour pressure corresponds to a saturated solution of metaboric acid in water.

Kracek *et al.*[1] have summarized and compared the data of prior workers; their summary is shown in Figs. 10 and 11. In addition, they have fitted equations to the data of some earlier workers. For the data of Bezzi[91] they present for the dissociation of H_3BO_3 to HBO_2(II) the equation:

$$\text{Log } P(\text{mm}) = -12{,}350/4{\cdot}574\, T + 1{\cdot}75 \text{ Log } T + 4{\cdot}8115.$$

Bezzi has also presented additional data bearing on the problem.[92, 93] Kracek *et al.*[1] have fitted the data of Gilbert and Levi[94] for the dissociation of H_3BO_3 to HBO_2(III), yielding the equation:

$$\text{Log } P(\text{mm}) = -13{,}940/4{\cdot}574\, T + 2 \text{ Log } T + 4{\cdot}8254.$$

Table XIVe.—Thermodynamic Functions for Metaboric Acid (HBO_2) (Ideal Gas) mol wt=43·828[89]

	cal/(mol deg)			kcal/mol			
T, K	C°_p	S°	$\frac{-(F^\circ-H^\circ_{298})}{T}$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_P
0	0·000	0·000	Infinite	−2·554	−133·175	−133·175	Infinite
100	7·984	47·787	65·377	−1·759	−133·478	−132·878	290·390
200	8·816	53·517	58·155	−0·928	−133·709	−132·196	144·450
298	10·094	57·273	57·273	0·000	−134·000	−131·395	96·310
300	10·118	57·336	57·273	0·019	−134·006	−131·379	95·705
400	11·366	60·420	57·686	1·094	−134·311	−130·457	71·275
500	12·466	63·078	58·504	2·287	−134·611	−129·459	56·584
600	13·402	65·436	59·466	3·582	−134·896	−128·401	46·768
700	14·189	67·562	60·474	4·962	−135·161	−127·297	39·742
800	14·851	69·502	61·483	6·415	−135·404	−126·159	34·463
900	15·414	71·284	62·474	7·929	−135·626	−124·989	30·350
1000	15·895	72·934	63·438	9·495	−135·831	−123·795	27·054
1100	16·311	74·469	64·372	11·106	−136·026	−122·583	24·354
1200	16·671	75·904	65·274	12·756	−136·210	−121·351	22·100
1300	16·986	77·251	66·144	14·439	−136·390	−120·106	20·191
1400	17·260	78·520	66·983	16·151	−136·566	−118·847	18·552
1500	17·501	79·719	67·793	17·890	−136·742	−117·575	17·130
1600	17·713	80·856	68·574	19·651	−136·920	−116·292	15·884
1700	17·901	81·935	69·328	21·432	−137·100	−114·996	14·783
1800	18·066	82·963	70·057	23·230	−137·284	−113·691	13·803
1900	18·214	83·944	70·763	25·044	−137·471	−112·376	12·926
2000	18·345	84·882	71·445	26·872	−137·659	−111·051	12·135
2100	18·462	85·779	72·107	28·713	−137·851	−109·713	11·417
2200	18·567	86·641	72·748	30·564	−138·047	−108·370	10·765
2300	18·661	87·468	73·370	32·426	−138·246	−107·017	10·168
2400	18·746	88·264	73·974	34·296	−138·451	−105·652	9·620
2500	15·822	89·031	74·561	36·175	−144·049	−104·176	9·107
2600	18·892	89·771	75·132	38·060	−144·256	−102·576	8·622
2700	18·955	90·485	75·688	39·953	−144·465	−100·968	8·172
2800	19·012	91·175	76·228	41·851	−144·676	−99·354	7·755
2900	19·065	91·843	76·755	43·755	−144·889	−97·726	7·364
3000	19·113	92·490	77·269	45·664	−145·105	−96·099	7·000
3100	19·156	93·118	77·770	47·577	−145·323	−94·464	6·659
3200	19·197	93·727	78·260	49·495	−145·544	−92·821	6·339
3300	19·234	94·318	78·737	51·417	−145·768	−91·168	6·037
3400	19·268	94·893	79·204	53·342	−145·995	−89·511	5·753
3500	19·300	95·452	79·660	55·270	−146·225	−87·849	5·485
3600	19·329	95·996	80·107	57·202	−146·458	−86·175	5·231
3700	19·356	96·526	80·543	59·136	−146·696	−84·497	4·991
3800	19·381	97·042	80·971	61·073	−146·935	−82·808	4·762
3900	19·404	97·546	81·389	63·012	−147·178	−81·123	4·546
4000	19·426	98·038	81·799	64·954	−268·603	−77·283	4·222
4100	19·447	98·518	82·201	66·897	−268·621	−72·500	3·864
4200	19·466	98·986	82·595	68·843	−268·641	−67·709	3·523
4300	19·483	99·445	82·982	70·790	−268·665	−62·927	3·198
4400	19·500	99·893	83·361	72·739	−268·694	−58·145	2·888
4500	19·516	100·331	83·733	74·690	−268·725	−53·359	2·591
4600	19·530	100·760	84·099	76·643	−268·758	−48·567	2·307
4700	19·544	101·180	84·458	78·596	−268·796	−43·779	2·036
4800	19·557	101·592	84·810	80·551	−268·837	−38·991	1·775
4900	19·569	101·995	85·157	82·508	−268·881	−34·208	1·526
5000	19·581	102·391	85·498	84·465	−268·928	−29·420	1·286
5100	19·592	102·779	85·833	86·424	−268·980	−24·626	1·055
5200	19·602	103·159	86·162	88·384	−269·033	−19·836	0·834
5300	19·612	103·533	86·487	90·344	−269·089	−15·042	0·620
5400	19·621	103·899	86·806	92·306	−269·151	−10·250	0·415
5500	19·630	104·260	87·120	94·268	−269·213	−5·452	0·217
5600	19·638	104·613	87·429	96·232	−269·281	−0·660	0·026
5700	19·646	104·961	87·734	98·196	−269·351	4·137	−0·159
5800	19·654	105·303	88·034	100·161	−269·425	8·937	−0·337
5900	19·661	105·639	88·329	102·127	−269·502	13·736	−0·509
6000	19·668	105·969	88·620	104·093	−269·583	18·543	−0·675

Dec. 31, 1960; Mar. 31, 1961; June 30, 1963; Dec. 31, 1964

Table XIVf.—Thermodynamic Functions for Metaboric Acid, Trimeric ($(HBO_2)_3$), (Ideal Gas) mol wt = 131·484[89]

	cal/(mol deg)			kcal/mol			
T, K	C_p°	S°	$\frac{-(F^\circ-H^\circ_{293})}{T}$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	0·000	0·000	Infinite	−5·440	−538·303	−538·303	Infinite
100	12·319	60·120	105·418	−4·530	−540·688	−530·561	1159·485
200	23·148	71·939	85·750	−2·762	−542·105	−519·844	568·032
298	32·807	83·047	83·047	0·000	−543·000	−508·717	372·882
300	32·969	83·250	83·048	0·061	−543·013	−508·505	370·428
400	40·477	93·820	84·438	3·753	−543·461	−496·924	271·494
500	45·833	103·463	87·294	8·084	−543·610	−485·268	212·100
600	49·633	112·174	90·727	12·868	−543·566	−473·601	172·501
700	52·405	120·044	94·363	17·977	−543·392	−461·951	144·221
800	54·509	127·185	98·026	23·327	−543·130	−450·338	123·021
900	56·170	133·704	101·633	28·864	−542·801	−438·757	106·540
1000	57·522	139·695	105·144	34·551	−542·427	−427·212	93·363
1100	58·648	145·231	108·540	40·361	−542·035	−415·712	82·590
1200	59·602	150·377	111·815	46·274	−541·624	−404·245	73·619
1300	60·418	155·180	114·968	52·276	−541·211	−392·814	66·035
1400	61·123	159·684	118·002	58·354	−540·797	−381·413	59·538
1500	61·735	163·923	120·924	64·498	−540·398	−370·046	53·913
1600	62·270	167·924	123·738	70·699	−540·014	−358·700	48·994
1700	62·740	171·714	126·449	76·950	−539·645	−347·377	44·656
1800	63·153	175·312	129·065	83·245	−539·297	−336·081	40·804
1900	63·519	178·736	131·590	89·579	−538·966	−324·798	37·359
2000	63·844	182·003	134·029	95·947	−538·647	−313·537	34·260
2100	64·133	185·125	136·389	102·346	−538·344	−302·285	31·458
2200	64·392	188·115	138·672	108·773	−538·062	−291·053	28·912
2300	64·623	190·982	140·885	115·224	−537·792	−279·833	26·589
2400	64·832	193·737	143·030	121·697	−537·546	−268·615	24·460
2500	65·020	196·387	145·112	128·190	−553·482	−257·096	22·474
2600	65·190	198·941	147·133	134·700	−553·248	−245·243	20·614
2700	65·344	201·404	149·098	141·227	−553·025	−233·397	18·891
2800	65·484	203·783	151·009	147·768	−552·813	−221·568	17·293
2900	65·611	206·083	152·868	154·323	−552·609	−209·727	15·805
3000	65·728	208·310	154·679	160·890	−552·417	−197·917	14·418
3100	65·835	210·466	156·444	167·469	−552·231	−186·103	13·120
3200	65·933	212·558	158·165	174·057	−552·060	−174·297	11·903
3300	66·023	214·588	159·845	180·655	−551·899	−162·490	10·761
3400	66·106	216·561	161·484	187·261	−551·750	−150·696	9·686
3500	66·183	218·478	163·085	193·876	−551·611	−138·908	8·673
3600	66·254	220·344	164·650	200·498	−551·482	−127·112	7·716
3700	66·319	222·160	166·180	207·126	−551·368	−115·325	6·812
3800	66·380	223·929	167·676	213·761	−551·261	−103·532	5·954
3900	66·437	225·654	169·141	220·402	−551·166	−91·766	5·142
4000	66·490	227·337	170·575	227·049	−914·621	−73·553	4·019
4100	66·539	228·979	171·979	233·700	−913·855	−52·533	2·800
4200	66·585	230·583	173·356	240·356	−913·096	−31·524	1·640
4300	66·628	232·151	174·705	247·017	−912·349	−10·545	0·536
4400	66·668	233·683	176·028	253·682	−911·617	10·412	−0·517
4500	66·706	235·181	177·326	260·351	−910·894	31·356	−1·523
4600	66·742	236·648	178·599	267·023	−910·178	52·300	−2·485
4700	66·775	238·084	179·850	273·699	−909·478	73·216	−3·404
4800	66·807	239·490	181·078	280·378	−908·786	94·124	−4·285
4900	66·836	240·868	182·284	287·060	−908·105	114·988	−5·128
5000	66·864	242·218	183·469	293·745	−907·434	135·864	−5·938
5100	66·890	243·543	184·634	300·433	−906·777	156·733	−6·716
5200	66·915	244·842	185·780	307·123	−906·126	177·567	−7·463
5300	66·939	246·117	186·906	313·816	−905·484	198·413	−8·181
5400	66·961	247·368	188·014	320·511	−904·858	219·219	−8·872
5500	66·982	248·597	189·104	327·208	−904·235	240·054	−9·538
5600	67·003	249·804	190·178	333·908	−903·630	260·828	−10·179
5700	67·022	250·990	191·234	340·609	−903·034	281·623	−10·797
5800	67·040	252·156	192·274	347·312	−902·448	302·407	−11·394
5900	67·057	253·302	193·299	354·017	−901·870	323·173	−11·971
6000	67·074	254·429	194·309	360·723	−901·305	343·941	−12·527

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1964

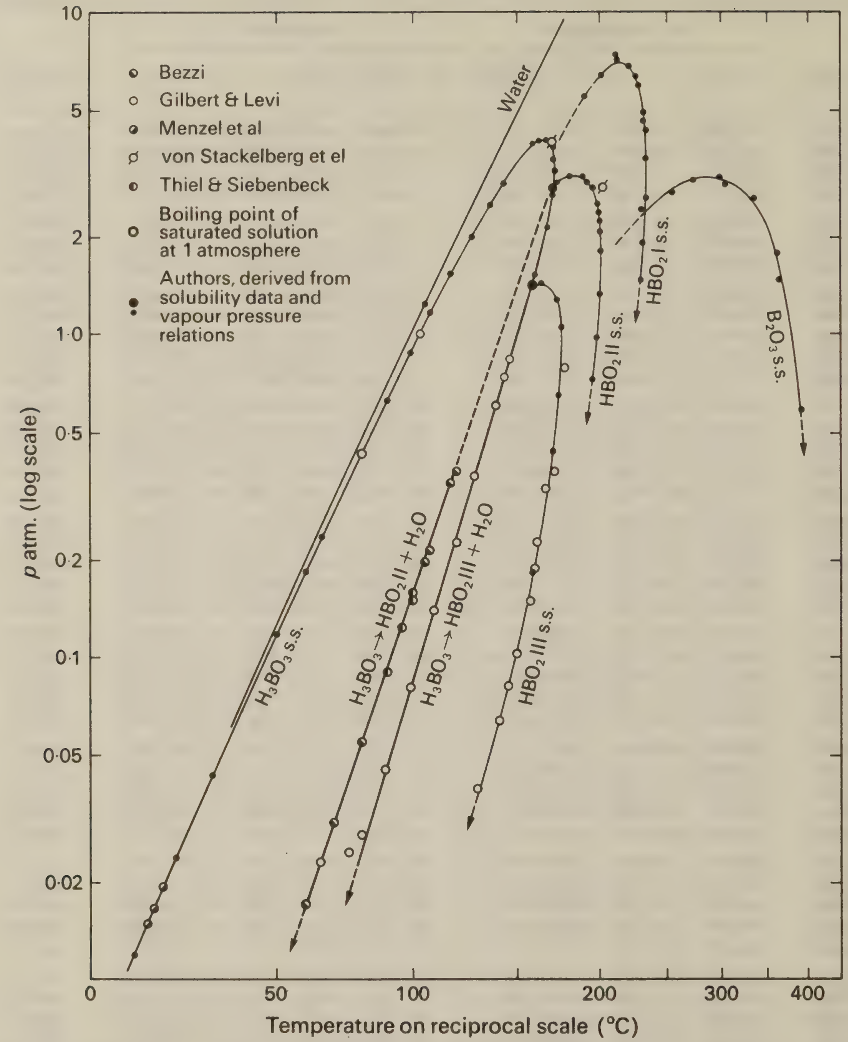


Fig. 10.—*P–T* diagram for the vapour pressures of saturated solutions in the system $H_2O–B_2O_3$[1]

The data of Tazaki[6, 7] are in fair agreement with those of Bezzi. As indicated in Fig. 10, the data of a number of workers[1, 3, 4, 6, 7, 91, 95, 96] provide reasonable agreement. Stackelberg and Quatram[96] have illustrated the phase relations for the system. Their illustration is reproduced in Fig. 12.

More recently the system $H_2O–B_2O_3$ has been examined at higher temperatures (> 1000 K),[18, 19, 28] by using transpiration and mass spectrometric[421] methods. The principal vaporization mechanism at these temperatures is concluded to be[18, 19]:

$$1/2H_2O(g) + 1/2B_2O_3(s) \rightleftharpoons HBO_2(g).$$

Fig. 13 shows a plot of log K for the reaction versus $1/T$.[18]

The process of dehydrating the boric acids, which is related to the vapour pressures in the system $B_2O_3–H_2O$, has been studied by a variety of techniques.[11, 97, 109, 369, 370] Differential thermal analysis has been used to study kinetics[422] and dehydration mechanisms.[423] Curves for simultaneous D.T.A. and thermogravimetric analysis at

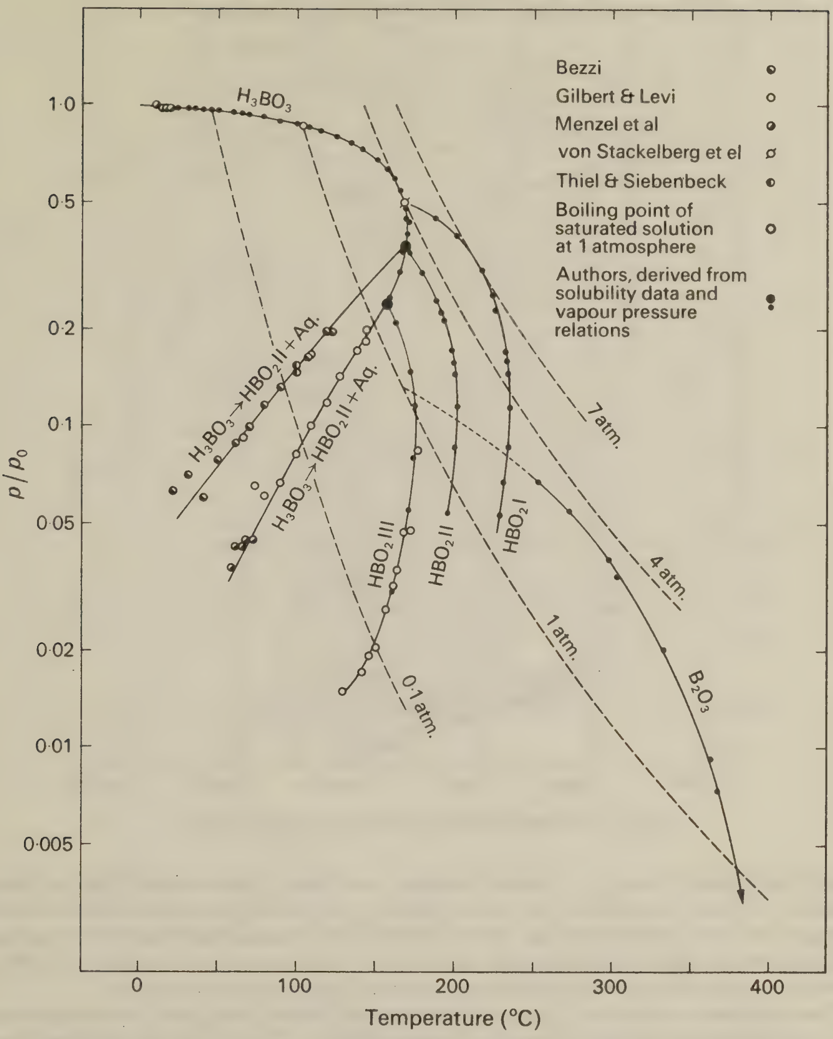


FIG. 11.—Relative vapour pressure and temperature relations for the saturated solutions in the system H_2O–B_2O_3. Experimental points are marked same as in Fig. 10[1]

atmospheric pressure are shown in Fig. 14[109]; similar studies have been made at reduced pressure.[98] Boric acid has been suggested as a standard material for calibrating thermogravimetric balances.[96] The activation energy for the dehydration of boric acid has been estimated from thermogravimetric studies as 10·1[102] and 143[105] kcal/mol. The merits of such methods have been critically reviewed.[422]

The use of organic liquids as a means of controlling the temperature during dehydration of boric acid and removing the water by azeotropic distillation has received considerable attention.[99, 100, 106–8] The process is often carried out in two stages, and it is claimed that the rate of the process is controlled by the diffusion rate of water through the boric acid particles.[99, 100, 107] Dehydration of orthoboric to metaboric acid in this way was found to be of zero order with respect to orthoboric acid at high temperatures and with finely ground powder.[430]

Because hydration or dehydration is part of the volatilization process for the boric acids, the presence of water from an outside source, such as a steam generator or

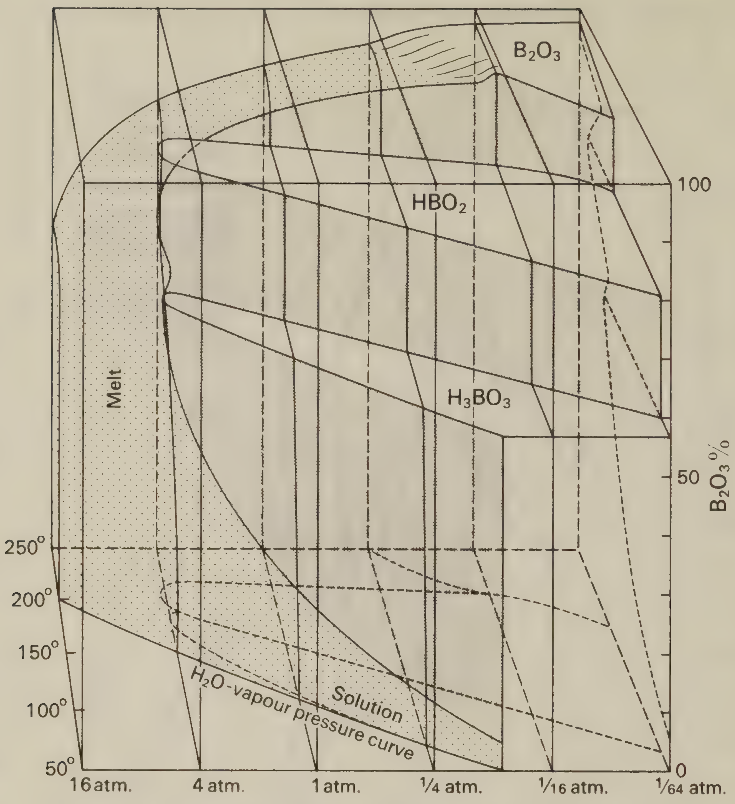


FIG. 12.—Phase relations in the system B_2O_3–H_2O[96]

simply the solvent water of a dilute solution, can have a pronounced effect on their volatility. In this same sense, the total pressure, to the degree that it involves water vapour, also has a strong effect. These factors have special significance for nuclear reactors, where boric acid solutions are used as 'nuclear shim', and for analytical chemistry, where it may be desirable to evaporate solutions of boric acids.

There has been controversy over the potential for loss of boric acid during evaporative procedures in analytical chemistry. Some workers[110–13] have maintained that there is no loss of boric acid. The true situation appears to be that described by Feldman,[114] who pointed out that the loss of boric acid was only 5% when 50% of the solution had evaporated, but increased as evaporation proceeded. Kronstrikin and Korovin[115] have explained this on the basis that the distribution of boric acid between solution and steam is in accordance with the expression:

$$C_v/C_w = K \text{ (a constant)}$$

with $K = 0{\cdot}005$. Thus if V kg of solution is evaporated to form D kg of vapour per hour, then in t hours the loss of boric acid is given by:

$$B = DtKC_w$$

The relative loss of boric acid for small amounts of evaporation is given by:

$$L = DtKC_w/VC_w = DtK/V$$

This expression indicates that 1 kilogram of solution boiled for 1 hour at a rate of

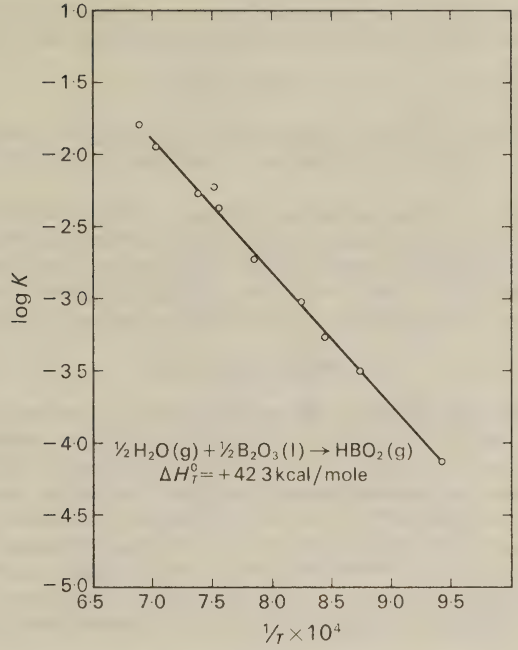


FIG. 13.—Plot of log K vs $1/T$ for reaction:
$\frac{1}{2}H_2O(g)+\frac{1}{2}B_2O_3(l) \rightarrow HBO_2(g)$[18]

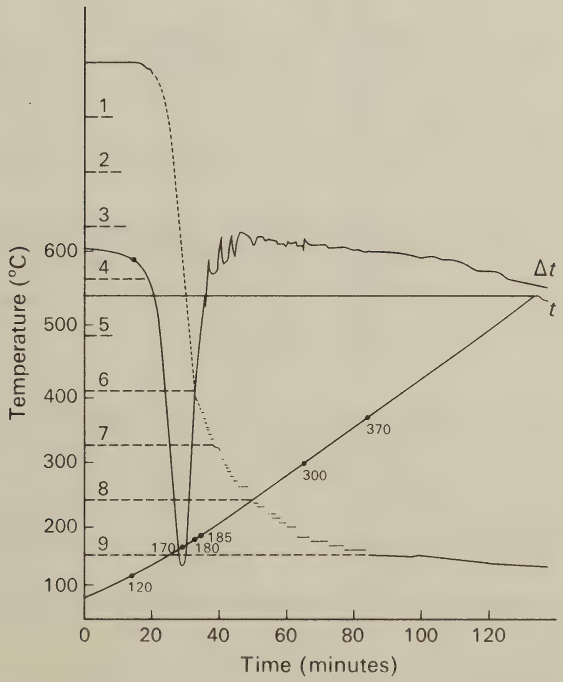


FIG. 14.—Simultaneous differential thermal analysis and gas liberation curves for boric acid, H_3BO_3[109]

0·2 kg/hour will lose 0·1% of its boric acid. However, when Dt is of the same order of magnitude as V, i.e. when much of the solution is evaporated, the expression becomes:

$$L = 1-\{V/(V-Dt)\}^{-K}$$

Under these conditions, the loss of boric acid is not negligible, and (so long as solid boric acid is not deposited) it is possible to volatilize most of the contained boric acid.

Russian workers have investigated the problem of the volatility of boric acid in steam over a wide range of pressures. They have also studied the effect of the presence of other salts or acids. The consensus seems to be that the distribution constant, K, relating the concentration of boric acid in the solution and in the vapour, varies as an exponential function of the densities of liquid and vapour, as in the expression:

$$K_d = C_v/C_w = (\rho_v/\rho_w)^n$$

This type of relationship holds for the distribution of a number of inorganic salts between solution and vapour phase, with water as the major constituent. Although there is agreement as to the form of the relationship, there are differences as to the value of the exponent, n. Styrikovich and co-workers favour the value 1·1 to 1·2[116–18] or 0·885.[119] Others suggest 0·9[120, 121] or 0·88.[122] Figures 15 and 16 show the results of Tskhvirashvili *et al.*[120] and Styrikovich *et al.*[119] Additional studies have been made under a variety of conditions.[123–30, 138, 10, 416, 417, 418] The effect of pH on the distribution constant is illustrated in Fig. 17, taken from Tskhvirashvili *et al.*[120] which shows that although the volatility is reduced in more basic solutions, there is still a significant effect.

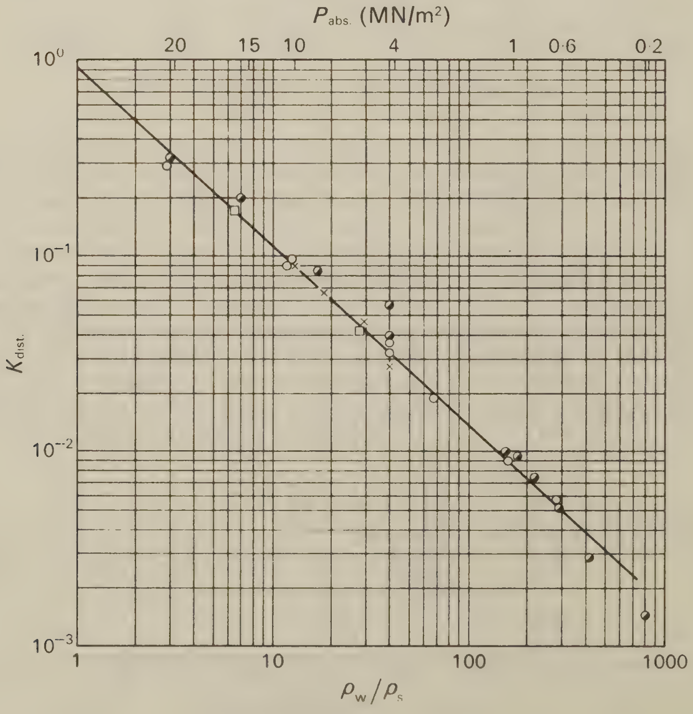


FIG. 15.—Distribution coefficients for boric acid as functions of the ratio densities of the water phases[120]

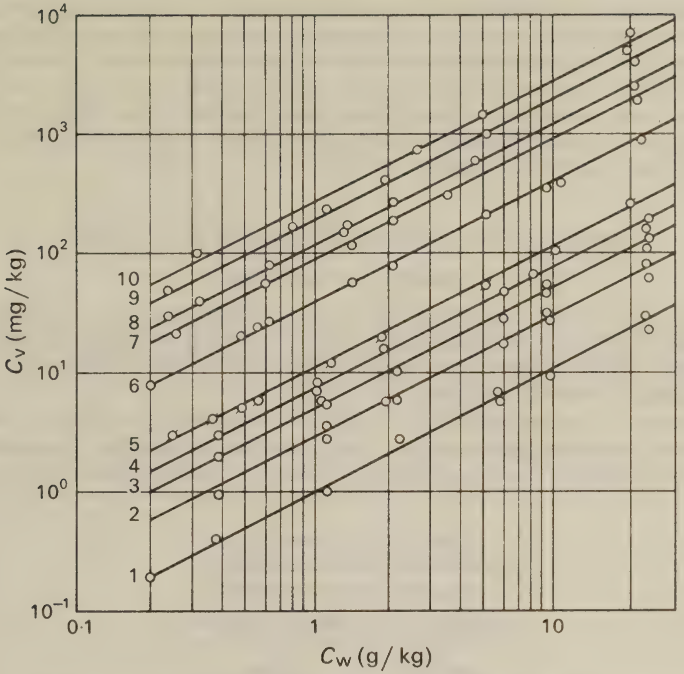


FIG. 16.—Variation in the solubility of boric acid in saturated steam with its content in water at the following pressures (in atm):
(1) $p=1$; (2) $p=3$; (3) $p=5$; (4) $p=7$; (5) $p=10$; (6) $p=40$; (7) $p=80$; (8) $p=100$; (9) $p=150$; (10) $p=200$[119]

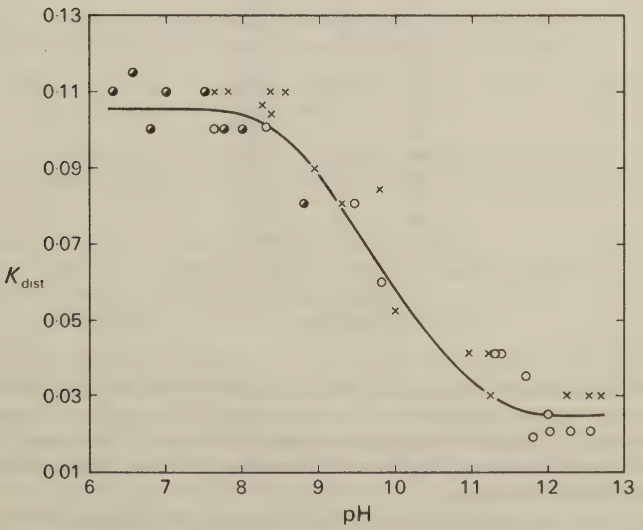


FIG. 17.—Variation of the apparent distribution coefficient $K^{\alpha}_{\rm dist}$ of boric acid as a function of the pH of the water at a gauge pressure of $P_e=10$ MN/m_2. Substances added to the water: ×—NaOH; ○—Na_3PO_4; ◑—$Ca(OH)_2$[120]

Boric acids have been proposed as materials to regulate the partial pressure of water vapour in semiconductor devices.[131, 132] Several investigators have studied the boron/chlorine ratio in the atmosphere as a means of following the volatilization from the oceans.[133–5] They have concluded that the boron results from a true evaporation, rather than from aerosol formation. Others have considered the effects of pH[136] of basin waters on the relative evaporation of boric acid and water, and the effect of boric acid on the evaporation of natural brines.[137]

AQUEOUS SOLUTIONS OF THE BORIC ACIDS

Solubility and its Effects

The solubility of boric acids in water is actually represented by a portion of the larger system B_2O_3–H_2O, as illustrated in Fig. 1,[1] covering the system at atmospheric pressure, and Fig. 12,[3] covering the system at elevated pressures; Benrath[141] presents additional data at elevated pressure.

The solubility of orthoboric acid in water at atmospheric pressure is a subject of special interest, which has been reported on and reviewed by a number of authors.[82, 142–5] The most recent results[145] are summarized in Table XV. Earlier studies are summarized in Mellor.[82] The solubility in water is affected by the presence of other compounds, sometimes being increased and sometimes decreased. The effect of sodium oxide, the most common additional component (present as borax), is discussed by Nies and Hulbert,[145] also in this volume, Section A9. The effects of other materials are discussed later under individual systems.

Table XV.—Solubility of Orthoboric Acid in Water[145]

Temp. °C	Wt % H_3BO_3
−0·76[a]	2·466
0	2·52
5	2·98
10	3·49
15	4·08
20	4·72
25	5·46
30	6·23
35	7·12
40	8·08
45	9·12
50	10·27
55	11·55
60	12·97
65	14·42
70	15·75
75	17·41
80	19·10
85	21·01
90	23·27
95	25·22
100	27·53
103·3[b]	29·27

[a] Cryohydric point.
[b] Boiling point.

The rate of solution of orthoboric acid in water was investigated,[146, 147] and found to increase in the presence of a surface-active agent.[147] The supersolubility limit ($T_s - T_c$), where T_s is the saturation temperature and T_c is the temperature of spontaneous crystallization, has been determined[148, 149]; the results are shown in Table XVI.

Table XVI.—Super Solubility Limits for Boric Acid

T_s	T_s–T_c	
	(Ref. 148)	(Ref. 149)
30	8·7	6·4
40	10·2	7·7
50	12·5	10·1
70	14·1	12·8

The heats of solution of the boric acids in water have been studied by a number of workers,[3, 150–4] and found to be endothermic. The results for orthoboric acid to form $H_3BO_3,500H_2O$ are summarized in Table XVII. The dependence of the molar heat of solution on molality (m) was found to fit the expression:

$$\Delta H = 234\, e^{-1230m} + 5273 - 53m \text{ (in cal/mol)}^{153}$$

This heat, of course, involves varying contributions from the heat of ionization, which are not large. For the metaboric acids, the heats of solution involve a heat of reaction to form orthoboric acid; Kilday and Prosen[150] find the following:

Table XVII.—Heats of Solution of Orthoboric Acid in Water

$H_3BO_{3(c)} + 500H_2O \rightarrow H_3BO_3.500H_2O$

ΔH kcal/mol	Reference
+5·3	3
+5·1 ± 0·05	151
+5·27	153
+5·17 ± 0·04	154
+5·26 ± 0·05	150
+5·45 + 0·02	152

$$HBO_2\ (c, \text{III}) + 1501\ H_2O \rightarrow H_3BO_3\ (1500\ H_2O);\ \Delta H = 0{\cdot}447 \pm 0{\cdot}045 \text{ kcal/mol}$$
$$HBO_2\ (c, \text{II}) + 901\ H_2O \rightarrow H_3BO_3\ (900\ H_2O);\ \Delta H = 1{\cdot}752 \pm 0{\cdot}053 \text{ kcal/mol}$$

They also measured the heats of solution in aqueous sodium hydroxide to yield solutions of sodium metaborate. Sokolova and Skuratov[155] also studied the heat of solution in water, and find;

$$HBO_2\ (c, \text{III}) + (n+1)\ H_2O \rightarrow H_3BO_3\ (nH_2O)$$
$$(n = 700,\ \Delta H = 0{\cdot}46 \pm 0{\cdot}01;\ n = 400,\ \Delta H = 0{\cdot}47 \pm 0{\cdot}01 \text{ kcal/mol}).$$
$$HBO_2\ (c, \text{II}) + (n+1)H_2O \rightarrow H_3BO_3(nH_2O)$$
$$(n = 500,\ \Delta H = 1{\cdot}76 \pm 0{\cdot}01 \text{ kcal/mol}).$$

An enthalpy–concentration chart for the system boric acid–water has been prepared.[162] The effect of the presence of other salts on the heat of solution of orthoboric acid is illustrated in Fig. 18.[156] The heat of dilution of boric acid solutions has been studied at 18° and 25°C[157]; the results are summarized in Table XVIII. It is seen that the heat increases with increasing concentration. Enthalpy of dilution varies linearly with molality to infinite dilution.[411] One additional value at still higher concentration is available as 68·3 cal/mol for dilution from 0·925 M to 0·006 M.[158] The isobaric heat capacities of dilute aqueous solutions have been determined.[407, 431]

The critical temperature of a 0·65 M boric acid solution is 386°C, an increase of 12·3°C over that of pure water.[159, 176]

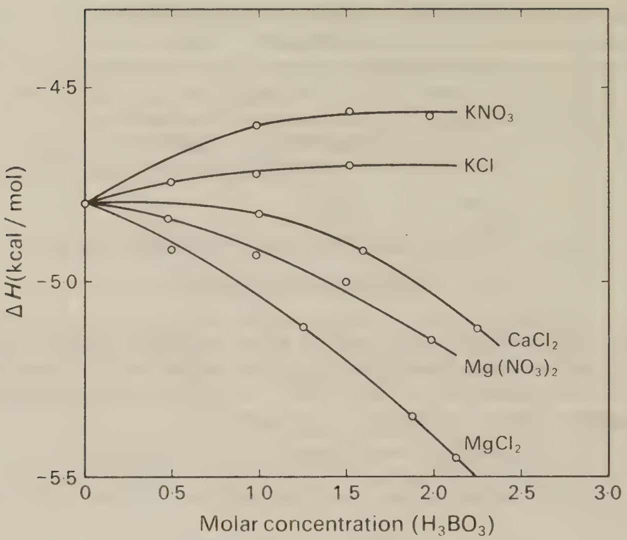


FIG. 18.—Effect of other salts on the heat of solution of orthoboric acid[156]

Table XVIII.—Measured Intermediate Heats of Dilution of Aqueous Solutions of Boric Acid at 25° and 18°C[157]

c_{init} (mol/litre)	c_{final} (mol/litre)	ΔH (cal/mol acid)	
		$t = 25°C$	$t = 18°C$
0·159	$3{\cdot}88 \times 10^{-3}$	−12·8	−13·5
0·159	$7{\cdot}65 \times 10^{-3}$	−12·3	−12·9
0·314	$7{\cdot}65 \times 10^{-3}$	−21·6	−22·6
0·314	$1{\cdot}52 \times 10^{-2}$	−21·1	−22·0
0·620	$1{\cdot}52 \times 10^{-2}$	−36·6	−43·4
0·620	$2{\cdot}98 \times 10^{-2}$	−35·3	−42·2

The density of aqueous boric acid solutions was studied at atmospheric pressure at temperatures of 16·9°, 20°, and 30°C for a range of concentrations[160]; the results are summarized in Table XIX. These data were used to derive the following relationship between density and temperature:

$$d_4^t = d_4^{20}\{1+\alpha(t-20)\}$$

where α is the coefficient of expansion, also shown in Table XIX. The density of the binary B_2O_3–H_2O liquid system with concentrations of from 4·9 to 83·0 mol-% B_2O_3 has more recently been measured, and the mean volume expansivity has been calculated.[412] The molar volume and the expansivity of this system are compared with those of other binary borates. The experimental results suggest a change in the boron-to-oxygen coordination number between the $3B_2O_3,H_2O$ and B_2O_3,H_2O compositions. The thermal expansivity of this system shows a different trend from those of alkali-borate melts. Densities of the solutions in the B_2O_3–H_2O system have been determined in the range 200–550°C.[413]

The partial molal volume of boric acid in water has been investigated over a much wider range of temperature and pressure.[161] The results are shown in Fig. 19, in which

Table XIX.—Density of Boric Acid Solutions[160]

Wt % H_3BO_3	$D_4^{16\cdot9}$	D_4^{20}	D_4^{30}	Cubic expansion coefficient	
				α 16·9°–20°	α 20°–30°
0·356	—	0·99973	—	—	—
0·892	1·00217	1·00137	0·99872	−2·60	−2·65
1·736	1·00568	1·00504	1·00227	−2·06	−2·88
2·174	—	1·00584	—	—	—
2·768	—	1·00809	—	—	—
3·773	—	1·01184	1·00893	—	−2·88
3·894	—	1·01223	—	—	—
4·599	—	1·01489	1·01175	—	−3·09

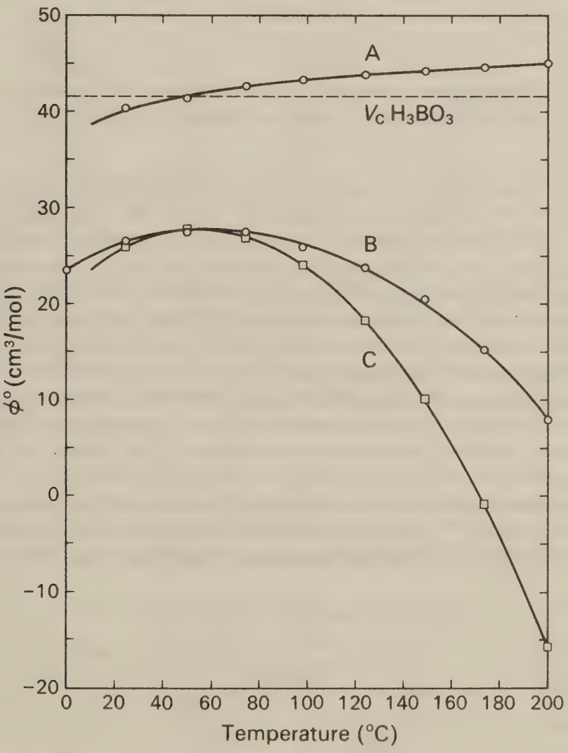


FIG. 19.—Variation with temperature of the partial molal volumes, $\phi°$, of (A) boric acid, (B) potassium chloride, and (C) barium chloride, A. von Endredy's results[161]

the behaviour of boric acid (essentially non-dissociated) is contrasted with that of the electrolytes KCl and $BaCl_2$. The partial molal volume is found to have no significant variation for concentrations ranging from 0·1 to 0·5 M, and is equal to the crystal molal volume at approximately 55°C, the temperature corresponding to maximum molal volume for many electrolytes in aqueous solution. Following a similar subsequent study, boric acid solute was said to behave as a 'structure breaker'.[463] The molal volume of boric acid in aqueous sodium chloride was found to be a linear function of concentration[464]; sodium chloride appeared to dehydrate H_3BO_3 and increase $B(OH)_3$–$B(OH)_3$ interactions.

Table XX.—Electrical Conductivity of Aqueous Boric Acid Solutions

Molar conc. H_3BO_3	18°C				40°C	
	X (10^6)		$\Lambda \times 10^2$		Ref. 166[a]	
	Ref. 166[a]	Ref. 167	Ref. 166	Ref. 167	$X \times 10^5$	$\Lambda \times 10^2$
0·0279	—	1·575	—	5·645	—	—
0·0561	—	2·395	—	4·269	—	—
0·0830	—	2·797	—	3·370	—	—
0·100	2·25	—	2·35	—	0·51	5·1
0·1122	—	3·222	—	2·872	—	—
0·1250	—	3·431	—	2·745	—	—
0·250	8·96	—	3·58	—	1·07	4·3
0·259	—	8·75	—	3·378	—	—
0·424	—	18·25	—	4·304	—	—
0·500	26·7	—	5·34	—	3·2	6·4
0·6020	—	32·28	—	5·362	—	—
0·75	60·5	—	8·07	—	6·5	8·6
1·0	—	—	—	—	11·5	11·5
1·25	—	—	—	—	17·6	13·2

[a] Values from ref. 166 are corrected for solution viscosity, those from ref. 167 are not.

The electrical conductivity of aqueous boric acid solutions has been studied at 18°C[166, 167] and 40°C[166]; the results are shown in Table XX. The significance of these measurements in understanding the state of boric acid in aqueous solution is discussed below under ionization. The polarographic behaviour of boric acid solutions has been attributed to the hydrogen ion produced by acid ionization.[199, 200] Electric conductivity was measured over the whole composition range of H_2O–B_2O_3 in the liquid state.[414] A peculiar conductivity–temperature relation was observed at low-to-intermediate B_2O_3 contents. The equivalent conductance of H_3BO_3 increases with its content in this range. Both the concentration of protons and its mobility through the proton-jump mechanism seem to change with the composition. The comparison of the results in the B_2O_3-rich range with those of alkali borates indicates a low extent of dissociation of the –B–O–H group.[414]

The dielectric constant of aqueous solutions of boric acid has been measured as a function of concentration.[168] The observed values show a minimum with concentration, as was also observed for other solutes studied. The results are illustrated in Fig. 20

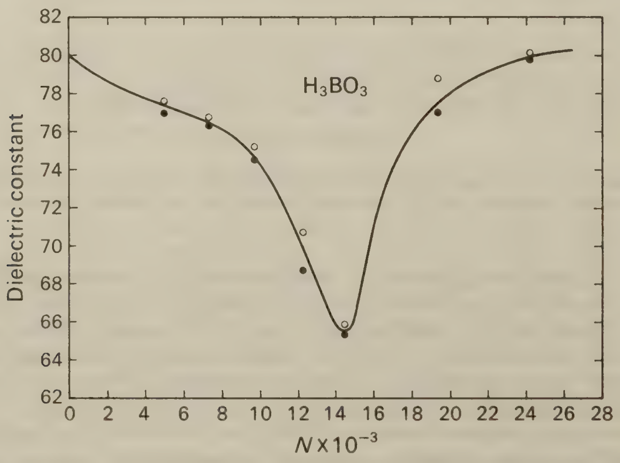


FIG. 20.—Dielectric constant of aqueous boric acid solutions[168]

Table XXa.—Dielectric Constant of Boric Acid Solution[168]

Boric Acid H_3BO_3

Conc. in %	Normality	Temp. in °C	ξ	ξ/ξ_0	ε	ε corrected
			Series I			
0·00	0·00000	21·5	2·48	1·000	80·0	80·0
0·10	0·00485	21·8	2·38	0·960	76·8	77·0
0·15	0·00728	21·8	2·36	0·952	76·2	76·4
0·20	0·00970	21·6	2·31	0·931	74·5	74·6
0·25	0·01213	21·6	2·13	0·859	68·7	68·8
0·30	0·01455	21·4	2·03	0·818	65·4	65·3
0·40	0·01940	21·3	2·45	0·988	79·0	78·8
0·50	0·02425	21·4	2·48	1·000	80·0	79·9
			Series II			
0·00	0·00000	21·2	0·679	1·000	80·0	80·0
0·10	0·00485	21·8	0·653	0·962	77·0	77·5
0·15	0·00728	21·8	0·648	0·954	76·3	76·8
0·20	0·00970	21·6	0·635	0·935	74·8	75·1
0·25	0·01213	21·6	0·598	0·881	70·5	70·8
0·30	0·01455	21·2	0·559	0·823	65·8	65·8
0·40	0·01940	21·0	0·655	0·965	77·2	77·0
0·50	0·02425	21·2	0·678	0·998	79·8	79·8

and Table XXa. They were interpreted[169] as indicating that in the concentration range near the minimum, most of the water molecules are held oriented in sheaths about the ions; for boric acid it is suggested that 183 molecules of water are bound per mole of boric acid and 1900 molecules per unit ionic charge. More recent measurements[170] were originally interpreted as measuring the rate of the ionization process. However, this conclusion was disputed,[171] and it appears that the initial results could not be confirmed.[172]

The thermal diffusion of boric acid in aqueous solution has been studied.[173–5] The results of Oholm are summarized in Table XXI. The thermal conductivity of aqueous boric acid solutions has been measured.[415]

Viscosity data for boric acid solutions have been reported.[419, 420]

Table XXI.—Thermal Diffusion Coefficients of Boric Acid[173]

Normality	*k* 20°C
0·05	0·954
0·1	0·876
0·5	0·826
1·0	0·816
1·5	0·813

Ionization in Aqueous Solution

It is well established that boric acid functions as a very weak acid in aqueous solution. However, the variation of pH with concentration indicates more complicated behaviour than that of a simple weak acid. Consequently a discussion of the ionization behaviour leads inevitably to considerations of the mechanism of ionization and the state of boric acid in aqueous solution.

Early studies of the interactions of boric acid solutions with acid-base indicators are discussed in Mellor.[82] Prideaux and Ward[177] measured the apparent dissociation constant of boric acid in various borate buffer solutions using a hydrogen electrode. They calculated an apparent ionization constant using the equation

$$k = Rh/(1-R)$$

where R is the ratio of equivalents of alkali to moles of acid.

In mixtures of borax and boric acid, k varies inversely with R, but the addition of sodium chloride increases k. In borax–boric acid mixtures k ranged from 3·6 to $6{\cdot}5 \times 10^{10}$.

From potentiometric titration studies using concentrated boric acid solutions and concentrated sodium hydroxide solutions, Hahn and Klockmann[216] calculated ionization constants for three stages of ionization to be

$$K_1 = (7{\cdot}3 \times 10^{-10})(f_1/f_{\mathrm{OH}}), \quad K_2 = (1{\cdot}8 \times 10^{-13})(f_2/f_{\mathrm{OH}}),$$

and

$$K_3 = (1{\cdot}6 \times 10^{-14})(f_2/f_{\mathrm{OH}}),$$

where f_1, f_2, and f_3 are the activity coefficients of the appropriate anion and f_{OH} is the activity coefficient for the hydroxide ion in the solution.

Kolthoff[166, 178–80] investigated the ionization by indicators and by electrical conductivity. From the electrical conductivity of 0·5 M boric acid solution he calculated an ionization constant of $8{\cdot}45 \times 10^{-9}$.[178] He also studied the effect of 0·5 M boric acid solution on the electrical conductivity of strong electrolytes and organic acids[178] and found a decrease in the ionic mobility of about 5–6% in all cases. Through the use of colorimetric indicators[166] he showed that in boric acid solutions the increase in hydrogen ion concentration with increasing boric acid concentration is greater than would be predicted from the ionization constant. He calculated ionization constants at 18°C and 40°C from the electrical conductivity values shown in Table XV, and at 60°C from e.m.f. measurements obtained by using a hydrogen electrode with a quinhydrone reference electrode. These values are summarized in Table XXII. He interpreted the results as indicating the formation of tetraboric acid (assumed to be a stronger acid) at concentrations above 0·1 M, and therefore the constant at 0·1 M applies to monomeric orthoboric acid. He found boric acid forms stable complex acids with organic hydroxy-acids[179] (see below). Kolthoff and Bosch[180] measured electrical conductivity and pH for mixtures of boric acid and sodium hydroxide at 18°C and 60°C. They found that in boric acid–borate mixtures with a large excess of boric acid over borate the pH increases abnormally on dilution, whereas in mixtures with a large excess of borate the pH decreases on dilution; for borax solutions the pH remains essentially constant on dilution. From these measurements they conclude that the best values for the ionization constant of orthoboric acid are $5{\cdot}5 \times 10^{-10}$ at 18°C, and $10{\cdot}6 \times 10^{-10}$ at 60°C.

Table XXII.—Ionization Constants of Boric Acid Solutions[166]

Molarity H_3BO_3	18°C	40°C	60°C
0·1	$4{\cdot}6 \times 10^{-10}$	$1{\cdot}2 \times 10^{-9}$	$6{\cdot}4 \times 10^{-10}$
0·25	26×10^{-10}	2·1	—
0·5	119×10^{-10}	9·4	14·4
0·75	408×10^{-10}	25·4	—
1·0	—	60·5	116
1·25	—	100×10^{-9}	—
1·5	—	—	564×10^{-10}

From studies of the preparation of air-stable, alkaline buffer solutions from orthoboric acid, potassium chloride, and sodium hydroxide, Fawcett and Acree[181] conclude the ionization constant of boric acid to be about $7{\cdot}5 \times 10^{-8}$.

Owen[182] determined the ionization constant of boric acid over a range of temperatures from cell measurements, using a cell of the type

$$H_2|HA(m_1),\ MA(m_2),\ MCl\ (m_3)|AgCl,Ag$$

His results are summarized in Table XXIII, showing the ionization constant and heat of ionization from 10° to 50°C. Jenkins[187] fitted Owen's data to the equation:

$$\text{Log } K = (140{,}600/T) + (125{,}782 \log T/T) - (29{,}371 \log^2 T/T) + 21{\cdot}5980$$

Branch *et al.*[183] determined the ionization constant of boric acid in water and in 25% by volume alcohol–water to be $6{\cdot}53 \times 10^{-10}$ and $1{\cdot}34 \times 10^{-10}$, respectively.

Table XXIII.—Ionization Constant and Heat of Ionization for Orthoboric Acid[182]

$t°$	$K \times 10^{10}$	ΔH (cal)
10	4·17	3920
15	4·70	3750
20	5·25	3570
25	5·80	3360
30	6·35	3140
35	6·89	2900
40	7·39	2630
45	7·89	2350
50	8·33	2040

Schafer and Sieverts[184] investigated the increase in ionization of boric acid solutions produced by the presence of neutral salts. They used a potentiometric titration technique applied to 0·0925 M boric acid solutions with up to 5 M neutral salt concentrations at 18°C. They found the increase in ionization depended upon the cation of the neutral salt, as shown in Table XXIV, summarizing the apparent ionization constant of boric acid in 2 M salt solutions. The effect of Ca^{2+} in enhancing the ionization is sufficient to allow boric acid to be titrated as a strong acid (using methyl red indicator) in saturated calcium chloride solution.

Table XXIV.—Apparent Ionization Constant of Orthoboric Acid in 2 M Neutral Salt Solutions[184]

Cation	$K \times 10^9$
K^+	0·9
Na^+	2·2
Li^+	5·0
Ba^{2+}	58
Sr^{2+}	110
Ca^{2+}	295

Owen and King[185] have studied the influence of sodium chloride concentration on the ionization for concentrations ranging from 0·02 to 3 M at temperatures from 5° to 55°C using the cell technique described previously.[182] They have calculated ionization constants as summarized in Table XXV, and the associated thermodynamic quantities summarized in Table XXVI. Mesmer and Baes measured boric acid–borate equilibria in aqueous potassium chloride by a concentration cell technique.[400]

Table XXV.—*Smoothed Values of* $-\log K^*$ *for Boric Acid in M-Molal Sodium Chloride Solutions*[185]

$t°$	$M = 0{\cdot}00$	0·02	0·07	0·36	0·725	1·25	2·00	3·00
5	9·438	9·318	9·237	9·089	9·024	8·985	8·976	9·005
10	9·380	9·260	9·180	9·034	8·970	8·934	8·926	8·956
15	9·328	9·207	9·127	8·982	8·920	8·885	8·878	8·908
20	9·280	9·158	9·078	8·934	8·874	8·840	8·834	8·863
25	9·237	9·114	9·034	8·891	8·831	8·798	8·791	8·820
30	9·198	9·074	8·994	8·850	8·791	8·758	8·752	8·779
35	9·163	9·038	8·957	8·814	8·754	8·721	8·714	8·739
40	9·132	9·006	8·924	8·780	8·720	8·687	8·679	8·701
45	9·104	8·978	8·895	8·750	8·689	8·655	8·646	8·665
50	9·081	8·952	8·869	8·722	8·661	8·626	8·614	8·630
55	9·060	8·931	8·846	8·697	8·635	8·598	8·585	8·597

Table XXVI.—*Thermodynamic Changes Accompanying the Ionization of Boric Acid at Infinite Dilution in M-Molal Sodium Chloride Solutions at 25°C*

M	ΔF^{0*}	ΔH^{0*}	$-\Delta C_p^{0*}$	$-\Delta S^{0*}$
0·00	12,597	3346	47·9	31·04
0·02	12,430	3415	45·3	30·24
0·07	12,320	3436	42·5	29·80
0·36	12,125	3413	34·9	29·22
0·725	12,044	3365	29·5	29·12
1·25	11,998	3323	23·6	29·10
2·00	11,990	3326	16·5	29·06
3·00	12,029	3438	7·2	28·82

Table XXVII.—*pK and Ionization Constants for Boric Acid from 0° to 60°C*[186]

Temperature °C	pK	$K \times 10^{10}$
0	9·5082	3·10
0	9·5074	3·11
5	9·4374	3·65
10	9·3785	4·18
15	9·3255	4·73
20	9·2780	5·27
25	9·2342	5·83
25	9·2337	5·84
30	9·1947	6·39
35	9·1605	6·91
40	9·1282	7·44
45	9·1013	7·92
50	9·0766	8·38
55	9·0537	8·84
60	9·0310	9·31

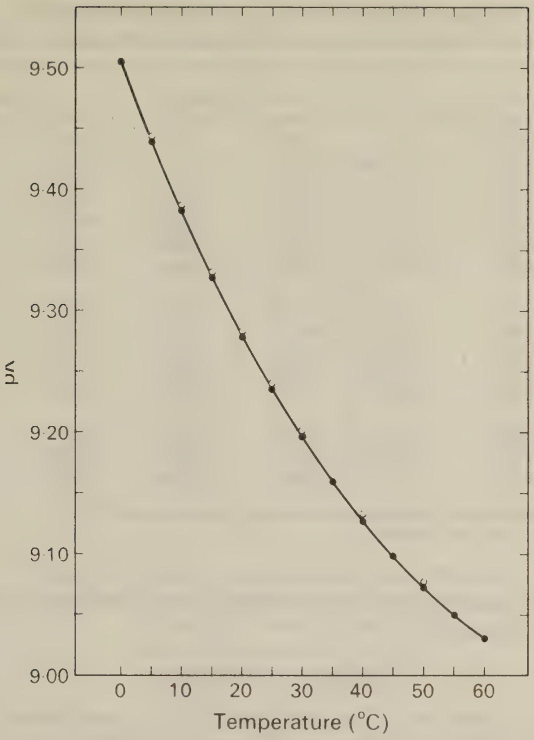


FIG. 21.—Variation of the thermodynamic ionization constant of boric acid from 0° to 60°C (closed circles).[186] (The open circles represent the data obtained by Owen[182])

Similar measurements have been made at the U.S. Bureau of Standards.[186] Their results for the ionization constant are summarized in Table XXVII and illustrated in Fig. 21. They find that the following equation for the ionization constant

$$pK = 2237{\cdot}94/T + 0{\cdot}016883T - 3{\cdot}305$$

where T = temperature in °K, reproduces the observed values of K to $\pm 0{\cdot}001$ unit except at the two extreme temperatures, where the discrepancy is about 0·006 unit. They present the following equations for thermodynamic quantities associated with the ionization process at infinite dilution:

$$\begin{aligned} \Delta F^\circ &= -RT\ln K = 2{\cdot}30259\, RTpK = 42{,}836 + 0{\cdot}032315\, T^2 - 63{\cdot}264\, T \\ \Delta S &= -(\partial \Delta F/\partial T)_p = -0{\cdot}64631\, T + 63{\cdot}3 \\ \Delta H^\circ &= \Delta F^\circ + T\Delta S^\circ = 42{,}836 - 0{\cdot}32315\, T^2 \\ \Delta C_p &= (\partial\, \Delta H^\circ/\partial T)_p = -0{\cdot}64631\, T \end{aligned}$$

They have also studied borax buffer solutions containing varying amounts of sodium chloride[215] with results summarized in Table XXVIIa.

Carpeni and co-workers investigated, over a period of years, the ionization of boric acid solutions.[188–93] They pointed out that the titration curves of boric acid solutions containing different concentrations of boric acid (but of constant ionic strength) all cross at a common point; that is, the curves are displaced in different directions at high and low pH regions.[188] This common intersection was defined as the isohydric point, that is, the point at which pH is independent of dilution.[189] The existence of this point (which was also observed for molybdic acid and germanic acid solutions) was interpreted as indicating the presence of a single equilibrium between two species, and two

Table XXVIIa.—Values for the Constants from 0° to 60°C in the Equations $pK' = pK'_0 + C\, m_{Cl}$ *and* $pK' = pK'_0 + D\, m_{Borax} + E\, m^2_{Borax}$ [215]

Temperature °C	$m_{Borax=0\cdot01}$		$m_{Borax=0\cdot025}$		$m_{Cl=0\cdot01}$		
	pK'_0	C	pK'_0	C	pK'_0	D	E
0	9·522	−0·23	9·545	−0·22	9·509	1·3	17
5	9·450	−0·22	9·479	−0·21	9·440	1·2	16
10	9·388	−0·21	9·417	−0·20	9·381	1·1	15
15	9·336	−0·20	9·360	−0·19	9·328	1·0	14
20	9·287	−0·19	9·308	−0·18	9·280	0·8	14
25	9·241	−0·18	9·259	−0·17	9·235	0·7	14
30	9·201	−0·17	9·222	−0·16	9·196	0·7	11
35	9·167	−0·16	9·187	−0·15	9·161	0·6	11
40	9·134	−0·16	9·155	−0·14	9·129	0·6	9
45	9·108	−0·15	9·122	−0·13	9·102	0·6	7
50	9·082	−0·14	9·094	−0·12	9·078	0·5	6
55	9·059	−0·13	9·072	−0·11	9·054	0·5	5
60	9·038	−0·12	9·049	−0·10	9·033	0·5	4

pK' = apparent ionization constant.

only.[189–93] At 20°C the isohydric point was found at pH 8·95 and was interpreted as corresponding to the equilibrium[191]:

$$K(H_2BO_3) \rightleftharpoons K_2(HB_5O_9),$$

with no evidence for tetraborate. The implications of this equilibrium for the structural behaviour of borates (solid and dissolved)[192] and the stability of the pentaborate in solution are discussed.[193] The significance of the isohydric point has been disputed by Souchay.[194]

Ripan and Liteanu[195, 196] have discussed the variation of pH with concentration in terms of mechanisms involving hydration of boric acid to form a strong acid, H_9BO_6, in concentrated solution.

Stetten[197] concluded from studies of the titration of various concentrations of boric acid and the variation of pH with concentration that boric acid polymerized in solution to yield species containing 3·2 molecules of boric acid, on average, which are stronger acids than boric acid itself; a non-integral average polymerization number implies that more than one polymeric species contributes to the acidity, as pointed out by Edwards.[198] Edwards measured pH in relatively concentrated boric acid solutions at 25°C, as shown in Table XXVIII; values calculated from electrical conductivity measurements are shown in Table XXVIIIa.[167] Under the assumption that all polymers contain only a single ionizable proton, analysis of the results is consistent with the idea that a trimer and a hexamer are the imporant polymeric forms. Values of the ionization constants for monomer, trimer and hexamer at 25°C are summarized in Table XXIX. The calculated pH of aqueous boric acid solutions as a function of temperature and added base content has been described.[419]

The effect of mono- and poly-hydroxy-compounds together with added salts has been studied by a titrimetric method.[230] In the presence of ethylene glycol the effects of added salts could be grouped into three classes:

Considerable increase in ionization: LiCl, $CaCl_2$, $BaCl_2$, NaBr, NaI, $Ca(NO_3)_2$, $Ba(NO_3)_2$.
Moderate increase in ionization: NaCl, $NaNO_3$, KBr, KI.
Little increase (*or decrease*) *in ionization:* KNO_3, Na_2SO_4, K_2SO_4.

The results are discussed in terms of salt effects on charge separation for tetrahedrally coordinated boron; when the cation is hydrated more than the anion the ionization of

Table XXVIII.—The Acidity of Concentrated H_3BO_3 Solutions $t = 25°C$; No Added Salt[177]

$[H_3BO_3]_9$ M	pH
0·753	3·69
0·663	3·815
0·603	3·92
0·512	4·065
0·452	4·16
0·422	4·22
0·361	4·35
0·301	4·49
0·241	4·63
0·211	4·71
0·1808	4·795
0·1507	4·89
0·1205	5·01
0·0904	5·14
0·0603	5·235
0·0301	5·32

Table XXVIIIa.—Hydrogen Ion Concentration in Boric Acid Solutions as Calculated from Electrical Conductivity[167]

Molarity H_3BO_3	$H^+ \times 10^6$
0·0279	4·59
0·0561	6·98
0·0830	8·16
0·1122	9·39
0·1250	10·00
0·2590	25·51
0·4240	53·21
0·6020	94·11

Table XXIX.—Ionization Constants for Boric Acid and Polymers at 25°C[198]

Constant	Series 'J'[a]	Series 'K'[a]	Series 'C–D'[b]
K	$3{\cdot}0 \times 10^{-10}$	$2{\cdot}7 \times 10^{-10}$	7×10^{-10}
K_3	$3{\cdot}4 \times 10^{-8}$	$3{\cdot}1 \times 10^{-8}$	13×10^{-8}
K_6	$1{\cdot}5 \times 10^{-7}$	$1{\cdot}4 \times 10^{-7}$	$\sim 12 \times 10^{-7}$

[a] No added salt; $t = 25{\cdot}0°$.
[b] 0·1 M K_2SO_4; $t = 25{\cdot}0°$; corrected for HSO_4^- using $1{\cdot}1 \times 10^{-2}$ as the acid ionization constant for HSO_4^-.

boric acid is increased, and when the anion is more strongly hydrated the reverse is true. Other workers have also studied the ionization of orthoboric acid in glycerol.[403]

Antikainen[201, 202] has studied the ionization of boric acid by potentiometric measurements. His interpretation of his own and Edwards's[198] results is in terms of the formation of a trimer and a tetramer of boric acid. He concludes that high concentrations of electrolytes and small concentrations of boric acid favour formation of the trimer, while low concentrations of electrolyte and high concentrations of boric acid favour formation of the tetramer. His results for pK_t in sodium perchlorate solutions are

Table XXX.—Boric Acid Ionization at 25°C[201, 202]

	Pure boric acid	0·1 M $NaClO_4$	3 M $NaClO_4$
pK_1	—	8·95	8·90
pK_3	7·450	—	6·725
pK_4	6·890	6·840	—

$K_1 = [H^+][B^-]/[HB]$, $K_3 = [H^+][B_3^-]/[HB]^3$, $K_4 = [H^+][B_4^-]/[HB]^4$.

Table XXXa.—Apparent Ionization of Boric Acid in Salt Solutions[201]

	Molarity		
	Salt	H_3BO_3	pK*
KCl	0·04980	0·2076	8·664
	0·04984	0·2781	8·427
	0·04978	0·4170	7·962
	0·04977	0·5282	7·674
	0·04985	0·7770	7·216
	0·09980	0·2078	8·595
	0·09950	0·2766	8·318
	0·09950	0·4176	7·913
	0·09973	0·5281	7·610
	0·09769	0·7766	7·145
NaCl	0·3980	0·4170	7·839
	0·3984	0·5278	7·527
	0·3981	0·7450	7·078
	0·3982	0·7771	7·028
	0·9926	0·4025	7·767
	0·9956	0·5276	7·425
	0·9967	0·7459	7·013
	0·9953	0·7725	6·954
	1·492	0·2781	8·062
	1·492	0·4090	7·699
	1·486	0·5275	7·381
	1·494	0·7714	6·915

summarized in Table XXX, and for sodium chloride solutions in Table XXXa. In similar studies Mesmer and Baes observed a reduction in the amount of polymerization as temperature increased.[400]

Lourijsen–Teyssedre[203] finds an ionization constant of 2×10^{-9} from pH titration studies extrapolated to infinite dilution, and interprets these results plus cryoscopic studies at the transition point of sodium sulphate, and studies of the partition of boric acid between water and alcohol, as indicating the presence of HBO_2, BO_2^-, $B_5O_8^-$, and $B_4O_7^{2-}$ in the aqueous solutions.

Sadek and Tadros[204] studied the optical density of mixtures of hydrochloric acid and orthoboric acid tinted with thymol blue, and also studied the pH of solutions of hydrochloric acid and orthoboric acid.[234, 235] They conclude that their results indicate that the reaction

$$H_3O^+ + H_3BO_3 \rightleftharpoons H_4BO_3^+ + H_2O$$

occurs in the solutions, with an energy equal to 0·524 eV for the transfer of a proton from water to boric acid. In a later publication they revise the value to 0·0683 eV.[205]

Ingri and co-workers have studied the ionization of orthoboric acid under a variety of conditions by potentiometric techniques.[206–9] In general their measurements were carried out in either sodium perchlorate solution to maintain constant ionic strength or in mixtures of sodium perchlorate and sodium hydroxide to maintain constant Na^+ concentration. In 3 M $NaClO_4$ solution at 25°C they conclude from measurements on orthoboric acid concentrations between 0·01 and 0·6 M[206] that the results are best interpreted in terms of the formation of $B(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$ as the principal anions. The ionization equations and associated constants are summarized as follows[206]:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+; \qquad \log K_{11} = -9{\cdot}00 \pm 0{\cdot}05$$
$$3B(OH)_3 \rightleftharpoons B_3O_3(OH)_4^- + H^+ + 2H_2O; \qquad \log K_{13} = -6{\cdot}84 \pm 0{\cdot}10$$
$$3B(OH)_3 \rightleftharpoons B_3O_3(OH)^{2-} + 2H^+ + H_2O; \qquad \log K_{23} = -15{\cdot}44 \pm 0{\cdot}20$$

(In reference 209 log K_{23} is changed to $-12{\cdot}00 \pm 0{\cdot}20$.)

As an alternative, the last equation may be replaced by

$$4B(OH)_3 \rightleftharpoons B_4O_4(OH)_6^{2-} + 2H^+ + H_2O; \quad \log K_{24} = -15{\cdot}71 \pm 0{\cdot}20$$

(In reference 209 log K_{24} is changed to $-13{\cdot}78 \pm 0{\cdot}20$.)

From additional measurements in 0·1 M $NaClO_4$ at 25°C[207] Ingri feels that the data between 0·01 and 0·2 M orthoboric acid are best explained in terms of the above equilibria, but at higher (0·4 M and 0·6 M orthoboric acid) concentrations an additional polynuclear complex, either $B_5O_5(OH)_3^-$ or $B_5O_6(OH)_4^-$ is required; he prefers the latter. The formation constants for these conditions are summarized in Table XXXI.

Table XXXI.—Equilibrium Constants, $^*\beta_{pq}$, with the Errors, 3 σ, Obtained by Using the Least Squares Programme LETAGROP on Data for Equilibria in Borate Solutions.[207] (The complexes AB^- ($^*\beta_1$), AB_3^- ($^*\beta_{13}$), AB_5^- ($^*\beta_{15}$) or AB_4^- ($^*\beta_{14}$) are formed from boric acid, B. All points have been given the weight, $w = 1$. B stands for $B(OH)_3$.)

Reaction	3 M $Na(ClO_4)$		0·1 M $Na(ClO_4)$	
	$\sim AB_4^-$	$\sim AB_5^-$	$\sim AB_4^-$	$\sim AB_5^-$
$B + H_2O \rightleftharpoons B(OH)^- + H^+$ $-\log {}^*\beta_1 \pm 3\sigma =$	$9{\cdot}00 \pm 0{\cdot}018$	$9{\cdot}00 \pm 0{\cdot}015$	$8{\cdot}98 \pm 0{\cdot}009$	$8{\cdot}98 \pm 0{\cdot}006$
$3B + H_2O \rightleftharpoons B_3(OH)^- + H^+$ $-\log {}^*\beta_{13} \pm 3\sigma =$	$6{\cdot}94 \pm 0{\cdot}051$	$6{\cdot}91 \pm 0{\cdot}028$	$7{\cdot}36 \pm 0{\cdot}042$	$7{\cdot}29 \pm 0{\cdot}015$
$4B + H_2O \rightleftharpoons B_4(OH)^- + H^+$ $-\log {}^*\beta_{14} \pm 3\sigma =$	$6{\cdot}96 \pm 0{\cdot}180$	—	$7{\cdot}14 \pm 0{\cdot}108$	—
$5B + H_2O \rightleftharpoons B_5(OH)^- + H^+$ $-\log {}^*\beta_{15} \pm 3\sigma =$	—	$6{\cdot}62 \pm 0{\cdot}156$	—	$6{\cdot}77 \pm 0{\cdot}102$
Standard deviation in Z, $\sigma(Z) =$	$\pm 0{\cdot}0024$	$\pm 0{\cdot}0021$	$\pm 0{\cdot}0016$	$\pm 0{\cdot}0011$

The results of ^{11}B nuclear magnetic resonance studies yield values in good agreement with these values. Figure 22[218] illustrates the distribution of boron among the various ions as a function of pH.

In studies using the 'self medium' method[210–12], involving the acidification of concentrated solutions of $B(OH)_4^-$ ions, the reaction

$$q\, B(OH)_4^- + pH_2O \rightleftharpoons H_pB(OH)_{4q}^{-q+p}$$

was examined. The acidification was followed to the point where an average of 0·05 H^+ ions were bound to each $B(OH)_4^-$ (assuming no hydrolysis). The results of these studies are summarized in Table XXXII.[208] Measurements were also made in 3 M NaBr, LiBr and KBr at orthoboric acid concentrations between 0·01 and 0·4 M. It was concluded that the principal species are $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and small amounts of $B_5O_6(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$, except that there is no evidence for the last species in 3 M KBr. These last results are summarized in Table XXXIII.

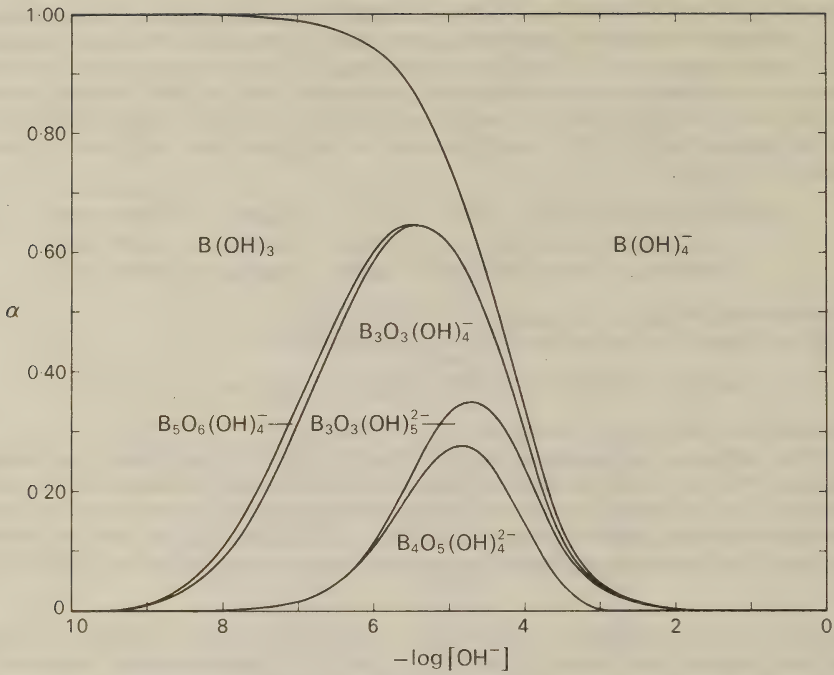


FIG. 22.—Distribution of boron between different ions. At a given log (OH⁻), the fraction of boron, α, present as a given ion, is represented by the segment of a vertical line falling within the corresponding range. Boric acid = 0·400 M[218]

Table XXXII.—Equilibrium Constants of Polyborates in $B(OH)_4^-$-medium[208]

B M	$\sigma(Z)$	$\log\beta_1 \pm 3\sigma$	$\log\beta_{24} \pm 3\sigma$	$\log\beta_{23} \pm 3\sigma$
0·6	±0·0020	5·227 ± 0·008	13·705 ± 0·034	—
	±0·0009	5·344 ± 0·015	14·021 ± 0·087	11·59 ± 0·13
1·2	±0·0020	5·211 ± 0·010	13·752 ± 0·043	—
	±0·0009	5·333 ± 0·015	13·969 ± 0·099	11·50 ± 0·10
2·5	±0·0025	5·217 ± 0·009	13·709 ± 0·036	—
	±0·0015	5·289 ± 0·027	13·878 ± 0·111	11·06 ± 0·27
3·0	±0·0024	5·223 + 0·011	13·673 ± 0·044	—
	±0·0016	5·271 ± 0·030	13·705 ± 0·138	11·00 ± 0·27
Mean values:		$5{\cdot}22_0 \pm 0{\cdot}01_0$	$13{\cdot}71_0 \pm 0{\cdot}03_9$	—
		$5{\cdot}30_9 \pm 0{\cdot}02_2$	$13{\cdot}89_3 \pm 0{\cdot}10_9$	11·29 ± 0·19

$$\beta_1 = [B(OH)_4^-][OH^-]^{-1}[B(OH)_3]^{-1}$$
$$\beta_{24} = [B_4O_5(OH)_4^{2-}][OH^-]^{-2}[B(OH)_3]^{-4}$$
$$\beta_{23} = [B_3O_3(OH)_5^{2-}][OH^-]^{-2}[B(OH)_3]^{-3}$$

Using the mean values we may calculate the constants for acidification of $B(OH)_4^-$

$$B(OH)_4^- \rightleftharpoons B(OH)_3 + OH^- \qquad \log K_1 \begin{cases} = -5{\cdot}22_0 \pm 0{\cdot}010 \\ = -5{\cdot}30_9 \pm 0{\cdot}022 \end{cases}$$
$$4B(OH)_4^- \rightleftharpoons B_4O_5(OH)_4^{2-} + 2OH^- + 5H_2O \qquad \log K_{24} \begin{cases} = -7{\cdot}17_0 \pm 0{\cdot}039 \\ = -7{\cdot}34_3 \pm 0{\cdot}109 \end{cases}$$
$$3B(OH)_4^- \rightleftharpoons B_3O_3(OH)_5^{2-} + OH^- + 3H_2O \qquad \log K_{13} = -4{\cdot}64 \pm 0{\cdot}19$$

Table XXXIII.—Formation Constants for Borates in 3 M Na(ClO_4), 3 M Na(Br), 3 M Li(Br) and 3 M K(Br)[209]

(The constants and the errors have been obtained by using the least squares programme LETAGROP. In the table, $\beta_1 = [B(OH)_4^-][B(OH)_3]^{-1}[OH^-]^{-1}$; $\beta_{13} = [B_3O_3(OH)_4^-][B(OH)_3]^{-3}[OH^-]^{-1}$; $\beta_{24} = [B_4O_5(OH)_4^{2-}][B(OH)_3]^{-4}[OH^-]^{-2}$; $\beta_{23} = [B_3O_3(OH)_5^{2-}][B(OH)_3]^{-3}[OH]^{-2}$ and so on.)

(In the first three calculations for Na(ClO_4) mainly polynuclear complexes are considered and the *B*-range used $\geq 0{\cdot}050$ M and in the fourth calculation all data (62 points) at low concentrations, $B \leq 0{\cdot}050$ M, and 58 points in the *B*-range $> 0{\cdot}050$ M have been used. Calculation for data $B \leq 0{\cdot}025$ M (the mononuclear curve) gave $\log \beta_1 \pm 3\sigma = 5{\cdot}24_8 \pm 0{\cdot}014$.)

Medium	Number of points	$\sigma(Z)$	$\log \beta_1$ $\pm 3\sigma$	$\log \beta_{13}$ $\pm 3\sigma$	$\log \beta_{24}$ $\pm 3\sigma$	$\log \beta_{23}$ $\pm 3\sigma$	$\log \beta_{15}$ $\pm 3\sigma$
Na(ClO_4)	120	0·0152	$5{\cdot}27_3 \pm 0{\cdot}021$	7·54 ± 0·08	—	12·09 ± 0·13	7·42
3·0 M	120	0·0113	$5{\cdot}28_4 \pm 0{\cdot}015$	7·47 ± 0·11	13·70 ± 0·08	—	7·42
	120	0·0095	$5{\cdot}27_4 \pm 0{\cdot}012$	7·41 ± 0·07	13·53 ± 0·12	11·67 ± 0·24	7·42 ± 0·70
	120	0·0097	$5{\cdot}25_3 \pm 0{\cdot}014$	7·38 ± 0·08	13·45 ± 0·13	11·96 ± 0·23	7·52
Na(Br)	114	0·0109	$5{\cdot}26_3 \pm 0{\cdot}012$	7·48 ± 0·06	—	12·17 ± 0·12	—
3·0 M	114	0·0094	$5{\cdot}26_9 \pm 0{\cdot}011$	7·26 ± 0·08	13·59 ± 0·10	—	—
	114	0·0069	$5{\cdot}26_4 \pm 0{\cdot}009$	7·35 ± 0·06	13·43 ± 0·12	11·86 ± 0·16	—
Li(Br)	100	0·0082	$5{\cdot}26_6 \pm 0{\cdot}008$	7·42 ± 0·06	—	12·16 ± 0·10	—
3·0 M	100	0·0080	$5{\cdot}26_7 \pm 0{\cdot}008$	7·17 ± 0·09	13·57 ± 0·10	—	—
	100	0·0059	$5{\cdot}26_6 \pm 0{\cdot}005$	7·29 ± 0·07	13·37 ± 0·16	11·88 ± 0·18	—
K(Br)	84	0·0106	$5{\cdot}10_6 \pm 0{\cdot}013$	7·38 ± 0·08	—	11·84 ± 0·15	—
3·0 M	84	0·0078	$5{\cdot}10_9 \pm 0{\cdot}010$	7·19 ± 0·08	13·41 ± 0·10	—	—
	84	0·0078	$5{\cdot}10_9 \pm 0{\cdot}010$	7·19 ± 0·08	13·41 ± 0·10	($\beta_{23} = -0{\cdot}69$)	—

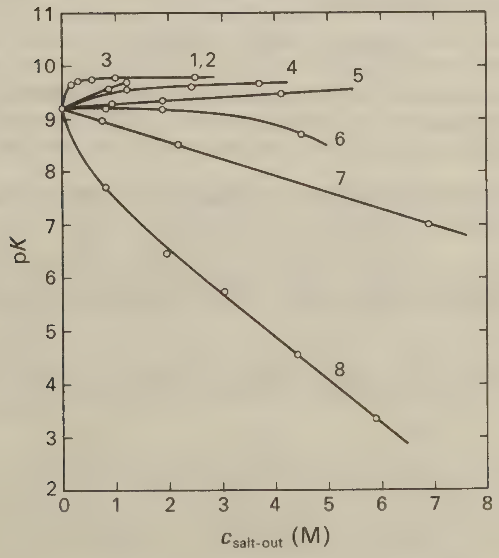


FIG. 23.—Variation of the p*K* of boric acid with the concentration of salting-out agents.[214] (1) Cæsium chloride; (2) cæsium iodide; (3) ethyl ether; (4) methanol; (5) potassium chloride; (6) sodium chloride; (7) lithium chloride; (8) calcium chloride

Frai and Ustyanovichova[213] measured pH and electrical conductivity at 20°C for solutions containing 0·01, 0·03 and 0·1 M orthoboric acid and from 0 to 0·4 M sodium hydroxide. They conclude that the first ionization constant is $6{\cdot}2 \times 10^{-10}$.

Vinogradov *et al.*[214] conducted potentiometric titrations of 0·16 M orthoboric acid in the presence of lithium, sodium, potassium, cæsium and calcium chlorides, cæsium iodide, methanol and ethyl ether. Their results are shown as the variation of pK with concentration of additive in Fig. 23.

The effect of pressure on the ionization of orthoboric acid in dilute solution in synthetic sea-water medium has been investigated.[217] The results, expressed as the ratio of the ionization constant at the measured pressure to that at one atmosphere pressure, are shown in Table XXXIV. Activity coefficients have been measured by isopiestic methods; indications were that boric acid behaves as a non-electrolyte.[424]

Table XXXIV.—Effect of Total Pressure on Boric Acid Ionization

P (atm)	$K_P/K_{1\ \mathrm{atm}}$
221	$1{\cdot}25 \pm 0{\cdot}01$
437	$1{\cdot}55 \pm 0{\cdot}01$
654	$1{\cdot}94 \pm 0{\cdot}01$

The rate of the ionization process in boric acid solutions is generally believed to be extremely high. It has been studied by polarographic techniques[219, 220], yielding a value of $k_d = 1{\cdot}3 \times 10^{-3}$/sec. Studies of dielectric dispersion[170] yielded a value of $k_d = 1{\cdot}3 \times 10^{10}$/(mol sec) at 35°C, but the data were found not to be reproducible.[172] Studies of the polymerization of borate ions by the 'temperature jump' method[218] have yielded results consistent with the assumption that the ionization rate constant must be in the order of 10^{10} mol/(litre sec), as estimated[218] by von Smoluchowsky's equation[221] for the specific rate of a diffusion-controlled reaction between one charged and one uncharged species, as in the equation

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^- ;$$

the equipment used could not, however, measure such high rates.

The rates of polymerization of boric acid ions, studied by the temperature jump method[218], have yielded values for the two polymerization reactions:

$$2B(OH)_3 + B(OH)_4^- \rightarrow B_3O_3(OH)_4^- + 3H_2O; \quad k_{23}.$$
$$2B(OH)_3 + B_3O_3(OH)_4 \rightarrow B_5O_6(OH)_4^- + 3H_2O; \quad k_{34}.$$

These are summarized in Table XXXV; the authors emphasize that the reaction for k_{23} is doubtless more complex than indicated by the equation and could easily involve

Table XXXV.—Over-all Rate Constants for Boric Acid

pH	k_{23} M^{-2}/sec	k_{34} M^{-2}/sec
5	4×10^4	
6	$7{\cdot}6 \times 10^3$	$4{\cdot}8 \times 10^2$
7·4	$2{\cdot}8 \times 10^3$	$2{\cdot}0 \times 10^2$
8	$3{\cdot}2 \times 10^3$	
9	$3{\cdot}2 \times 10^3$	
10	$3{\cdot}6 \times 10^3$	

three discrete bimolecular steps. However, too little information was available to estimate the rate in any further detail.

The rate of protonation of pyridine by various proton donors, including orthoboric acid, has been studied by polarographic techniques[228] over a range of temperatures and concentrations. The rate for orthoboric acid is lower than that for the hydrogen ion or veronal, but higher than for water. The rate of protonation of the phenylglyoxylate anion by various proton donors was also studied polarographically[232]; the rate constant for orthoboric acid at 25°C was $6{\cdot}38 \times 10^2$ litre/(mol sec). The rate of reaction of pellets of solid orthoboric acid with 0·05 N sodium hydroxide was studied under a variety of stirring conditions.[233]

Bell *et al.*[222] have provided an excellent discussion of the probable structures, acidity and ionization mechanism of boric acid solutions. They point out the following possible ionization mechanisms, where N is any Brønsted base, most probably water

1. $B(OH)_3 + N \rightleftharpoons BO(OH)_2^- + HN^+$
   $BO(OH)_2^- + H_2O \rightleftharpoons B(OH)_4^-$
2. $B(OH)_3 + H_2O \rightleftharpoons B(OH)_3(OH_2)$
   $B(OH)_3(OH_2) + N \rightleftharpoons B(OH)_4^- + HN^+$
3. $B(OH)_3 + H_2O + N \rightleftharpoons B(OH)_4^- + HN^+$
4. $H_2O + N \rightleftharpoons OH^- + NH^+$
   $B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^-$

It is not possible to select any of these as the most probable with currently available information. It seems clear, however, that the overall stoichiometry corresponds to

$$B(OH)_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_3O^+$$

and that the coordination number of boron changes from three to four as a consequence of the ionization process. A study of the kinetics of proton transfer appears also to favour this equation.[399] The Raman spectrum of aqueous borate solutions is consistent with the presence of a tetrahedral ion[66, 223–5], as is the ^{11}B nuclear magnetic resonance spectrum of borate solutions.[80, 226, 227] The mechanism of formation of polymeric species is discussed in terms of the reaction of neutral orthoboric acid molecules with the tetrahedral borate ion to form polymeric ions, rather than the polymerization of boric acid followed by ionization of the polymer.[80, 218] There appears to be no direct experimental evidence for the existence of unionized boric acid polymers in solution. Changes in the state of polymerization of borate ions in solution have been studied by means of infra-red absorption spectra.[231]

AQUEOUS SOLUTIONS OF BORIC ACID WITH ELECTROLYTES

Boric Acid–Inorganic Acid Systems

H_3BO_3–HNO_3–H_2O. Trombe has studied the system B_2O_3–HNO_3–H_2O, which includes the system with boric acids, at 30°C.[236] The results are summarized in Fig. 24. They indicate a minimum in the solubility in the neighbourhood of 30% nitric acid with some evidence that the solid phase is orthoboric acid. The solubility reaches a maximum for 91% nitric acid, and appears to represent an equilibrium with some form of metaboric acid.

H_3BO_3–H_2SO_4–H_2O (B_2O_3–SO_3–H_2O). The system of boric oxide with sulphur trioxide, with varying amounts of water, has received more attention than systems with other inorganic acids. Earlier work is reviewed in Mellor.[82] Levi and Gilbert[237] studied the system B_2O_3–SO_3—H_2O at 25°C and 45°C; they identified two new solid phases, $B_2O_3,SO_3,4H_2O$ and $3B_2O_3,SO_3,3H_2O$, by the Schreinemaker's method. They also measured densities of the saturated solutions. Their results are summarized in Table XXXVI and Fig. 25.

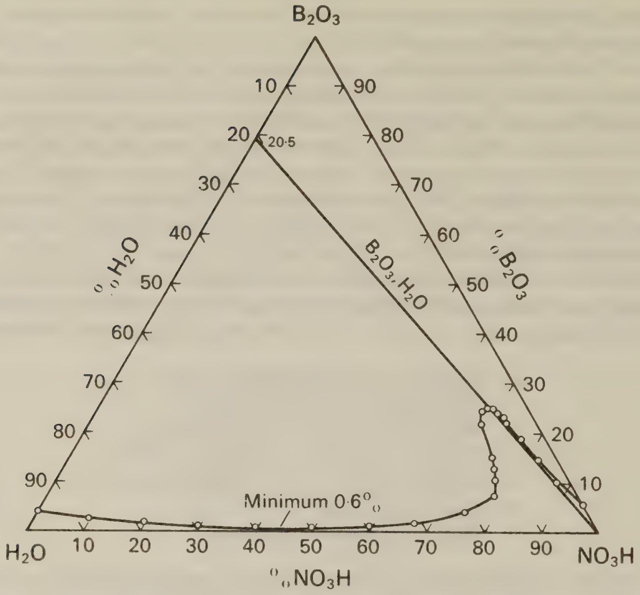


Fig. 24.—The system B_2O_3–HNO_3–H_2O at 30°C[236]

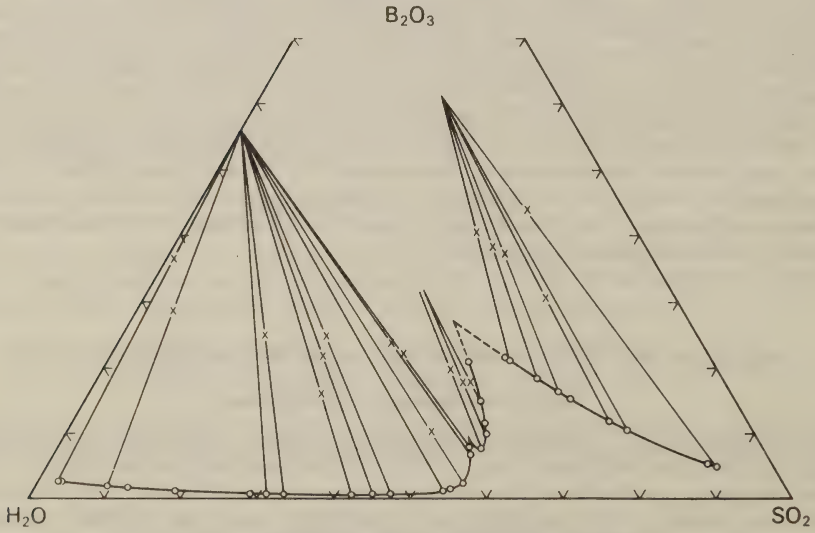


Fig. 25.—The system B_2O_3–SO_3–H_2O at 25°C[237]

Perova[246] has studied the system in greater detail in the water-rich region of composition and over a range of temperatures. His results are shown in Fig. 26. Additional data on the solubility of orthoboric acid in the water-rich regions is provided by Ferris and Kibby,[295] and Scholle and Machacova[281]; the data of the last authors are shown in Table XXXVIa.

More recently cryoscopic and electrical conductivity measurements in 100% sulphuric acid or dilute oleum[238] have provided convincing evidence that boric acids

Table XXXVI.—B_2O_3–SO_3–H_2O System[237]

(25°C)

$d_{4^\circ}^{25^\circ}$	Solutions Composition (g/100 g)		Wet solids Composition (g/100 g)		Solid phase
	SO_3	B_2O_3	SO_3	B_2O_3	
1·017	0·00	3·08			H_3BO_3
1·032	1·96	2·87	0·70	35·76	
1·039	2·90	2·79			
1·088	9·12	2·18	4·82	28·82	
1·112	11·85	2·00			
1·160	17·56	1·54			
1·270	28·82	1·04			
1·284	30·62	0·97	19·90	20·26	
1·305	32·78	0·87	18·94	24·78	
1·412	41·78	0·71	30·33	15·98	
1·446	44·44	0·68	27·74	21·60	
1·479	46·80	0·65	26·68	24·84	
	53·94	1·46	3·89	52·19	
	54·89	1·47			
1·625	55·84	2·69	47·22	10·79	
	54·66	6·09			
	54·16	7·17	35·30	23·98	
1·668	53·50	8·12	37·80	22·30	
	55·74	7·70	45·03	20·01	$B_2O_3,SO_3,4H_2O$
1·617	54·73	10·32	48·19	17·76	
	54·20	11·73			
	51·87	15·45	49·34	18·02	
	47·27	20·93			
	51·87	21·85			$3B_2O_3,SO_3,3H_2O$
	52·89	21·06	38·72	40·64	
	57·32	18·34	41·47	38·54	
	61·44	16·07	43·71	37·34	
	63·36	15·23			
	70·02	12·00	52·61	30·05	
1·882	73·66	10·39	59·50	24·90	
	86·24	5·07			
	86·50	4·96			
	87·72	4·82	43·43	43·45	

(45°C)

$d_{4^\circ}^{45^\circ}$	Solutions Composition (g/100 g)		Wet solids Composition (g/100 g)		Solid phase
	SO_3	B_2O_3	SO_3	B_2O_3	
1·023	0·00	5·17			
1·029	0·47	5·07	0·13	38·37	H_3BO_3
1·036	1·93	4·83	0·71	34·57	
1·086	8·58	3·74	4·86	28·88	
1·097	10·18	3·51	5·78	26·54	
1·231	25·48	1·89	15·48	23·33	
1·446	44·87	0·13	33·73	13·98	
1·628	52·25	7·07	37·81	20·52	
1·671	54·13	8·33	45·45	19·83	$B_2O_3,SO_3,4H_2O$
1·685	56·65	6·14	49·50	15·21	
	60·89	4·89	49·49	17·89	
	62·66	6·85	47·35	21·05	
1·800	57·22	13·56			
	59·87	23·60	41·08	35·18	$3B_2O_3,SO_3,3H_2O$
	57·70	19·25	41·34	40·29	
	60·43	17·99	46·64	35·66	

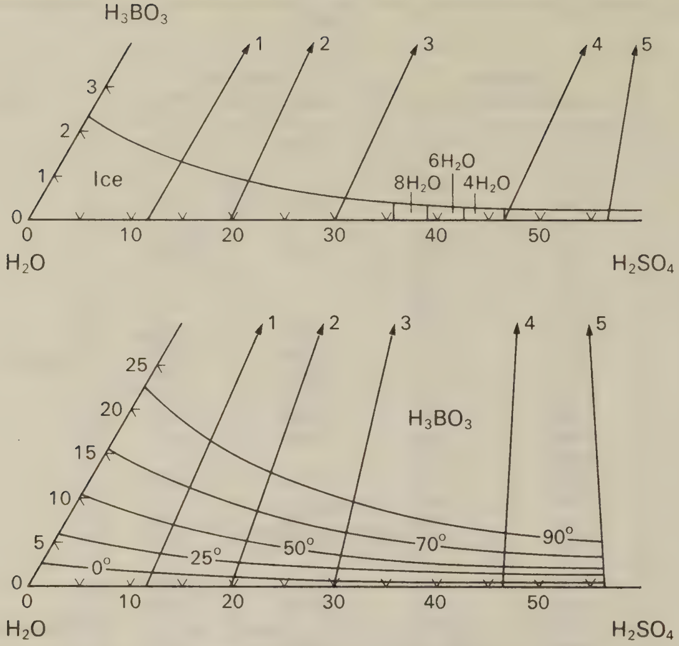


FIG. 26.—Isothermal triangle for H_3BO_3–H_2SO_4–H_2O[240]

Table XXXVIa.—System H_2SO_4–H_3BO_3–H_2O at 25°C[281]

Saturated solution % by weight		Wet residue % by weight		Solid phase
H_2SO_4	H_3BO_3	H_2SO_4	H_3BO_3	
—	5·48	—	—	H_3BO_3
9·49	4·09	2·10	66·34	H_3BO_3
10·48	4·06	5·18	53·21	H_3BO_3
18·50	2·76	7·16	70·78	H_3BO_3
20·01	2·86	10·17	51·14	H_3BO_3
29·73	1·79	10·60	63·44	H_3BO_3
38·64	1·20	21·59	37·64	H_3BO_3
40·60	1·59	22·60	50·64	H_3BO_3
48·91	0·94	13·18	64·36	H_3BO_3
49·95	1·43	28·25	44·02	H_3BO_3
54·44	1·21	33·98	38·36	H_3BO_3
57·33	1·15	32·68	44·12	H_3BO_3
58·48	1·35	13·51	71·03	H_3BO_3
67·27	2·78	30·29	57·49	H_3BO_3
67·13	3·02	35·68	58·64	$H_3BO_3 + H_2SO_4.2H_3BO_3$
70·39	2·65	43·42	56·26	$H_2SO_4.2H_3BO_3$
68·29	13·67	55·16	35·54	$H_2SO_4.2H_3BO_3$
67·05	18·33	59·03	31·54	$H_2SO_4.2H_3BO_3$
63·55	27·44	60·44	32·00	$H_2SO_4.2H_3BO_3$
64·00	28·00	—	—	$H_2SO_4.2H_3BO_3 \cdot$ $3H_2SO_4.4H_3BO_3$
67·16	23·86	60·75	33·39	$3H_2SO_4.4H_3BO_3$
69·22	22·63	54·95	44·39	$3H_2SO_4.4H_3BO_3$
—	—	55·76	42·97	$3H_2SO_4.4H_3BO_3$
68·41	4·78	57·84	19·16	H_3BO_3
66·96	10·18	—	—	H_3BO_3
66·37	11·32	—	—	H_3BO_3
65·54	14·42	46·30	39·60	H_3BO_3
61·17	22·12	19·73	63·64	H_3BO_3

and boric oxide all react on dissolving in sulphuric acid or dilute oleum to form the boron-tetra(hydrogensulphate) ion according to the equations:

$$B(OH)_3+6H_2SO_4 \rightarrow B(HSO_4)_4^- +3H_3O^+ +2HSO_4^-$$
$$B_2O_3+9H_2SO_4 \rightarrow 2B(HSO_4)_4^- +3H_3O^+ +HSO_4^-$$
$$B(OH)_3+3H_2S_2O_7 \rightarrow B(HSO_4)_4^- +H_3SO_4^+ H_2SO_4$$

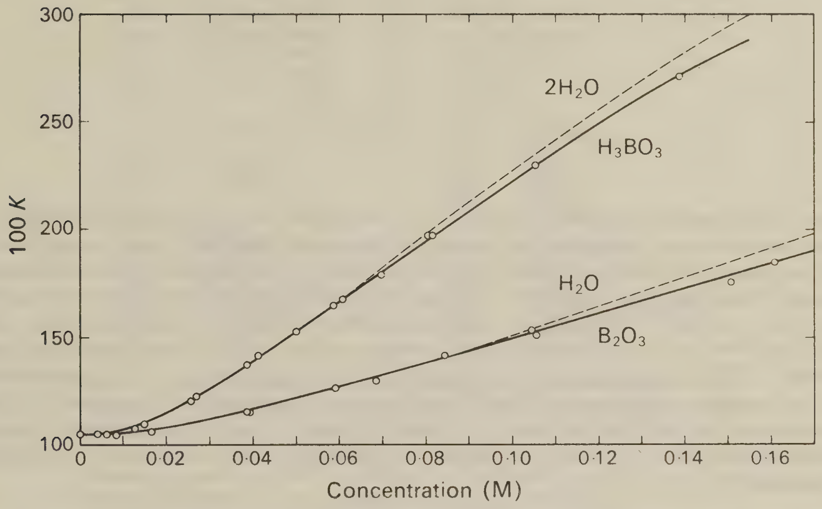


FIG. 27.—Specific conductances of solutions of boric acid and boric oxide in sulphuric acid[238]

Table XXXVII.—Specific Conductivities of Boric Acid Solutions in 100% Sulphuric Acid[240]

25°C				10°C			
W	10^2K	W	10^2K	W	10^2K	W	10^2K
$HB(HSO_4)_4$				$HB(HSO_4)_4$ (10·30°)			
0·0013	1·044	0·0608	1·683	0·0013	0·5863	0·0310	0·8039
0·0049	1·045	0·0031	1·048	0·0048	0·5864	0·0414	0·9098
0·0110	1·062	0·0076	1·055	0·0109	0·6062	0·0562	1·093
0·0172	1·103	0·0131	1·082	0·0171	0·6435	0·0796	1·318
0·0236	1·162	0·0181	1·131	0·0235	0·6977	0·0066	0·6070
0·0322	1·277	0·0223	1·182	0·0321	0·7960	0·0142	0·6544
0·0394	1·372	0·0507	1·525	0·0393	0·8745	0·0560	0·7605
0·0015	1·044	0·0348	1·294	0·0015	0·5868	0·0326	0·8234
0·0039	1·048	0·2198	3·652	0·0015	0·6467	0·0404	0·9016
0·0151	1·106	0·1175	2·682	0·0267	0·7502	0·0607	1·115
0·0268	1·223	0·1060	2·475	0·0425	0·9078	0·0075	0·603
0·0425	1·413	0·1175	2·661	0·0573	1·096	0·0131	0·624
0·0573	1·657	0·1338	2·839	0·0709	1·243	0·0181	0·669
0·0710	1·856	0·0743	1·888	0·0118	0·6328	0·0223	0·713
0·0118	1·089	0·0557	1·620	0·0218	0·7144		
0·0218	1·181	0·0970	2·213				
0·0316	1·284	0·0513	1·537				
0·0414	1·417	0·1142	2·577				
0·0562	1·655	0·1228	2·719				
0·0796	1·965	0·2900	4·084				
0·0062	1·063	0·1755	3·255				
0·0143	1·115	0·2548	3·849				
0·0256	1·235	0·3201	4·208				
0·0327	1·262	0·2530	3·871				
0·0404	1·407						

Table XXXVIII.—Densities of Solutions of Boric Acid in 100% Sulphuric Acid at 25°C

mol/kg 50 ln w	$HB(HSO_4)_4$
0·05	1·831
0·10	1·835
0·15	1·840
0·20	1·844
0·25	1·849
0·30	1·853

The boron tetra(hydrogensulphate) ion is analogous to the borate ion $B(OH)_4^+$ in aqueous solutions. However, the corresponding acid, $HB(HSO_4)_4$ is a strong acid in the sulphuric acid medium, and solutions of boric acid or boric oxide can be titrated directly with the base K_2SO_4.[238] The specific conductance of solutions of boric acid and boric oxide in sulphuric acid are illustrated in Fig. 27[238] and shown in Table XXXVII.[240] The densities of solutions of boric acid in sulphuric acid have been determined at 25°C[239] and are shown in Table XXXVIII as a function of the concentration of the resulting strong acid, $HB(HSO_4)_4$. On the assumption that the density of these solutions varies with temperature in the same manner as those of sodium and potassium hydrogen sulphate solutions, the density in the temperature range 0–40°C is given by the equation:

$$\rho_t = \rho_{25} + (1{\cdot}08 \times 10^{-3})(25 - t) \quad \text{where } t \text{ is temperature in °C.}$$

The Raman spectrum of solutions of boric acid in sulphuric acid solution has been observed and interpreted.[241] The results are presented in Table XXXIX. They indicate the occurrence of relatively large concentrations of disulphuric acid in concentrated solutions of boric acid or boric oxide. It is suggested that this results from a condensation process between tetra(hydrogensulphate) and borate ions to form polymeric ions containing B–O–B linkages as illustrated in Fig. 28, somewhat analogous to the polymeric ions formed in water solution. In further studies with concentrated solutions[247] various solid salts were isolated. They are suggested to contain higher polymers of boron–sulphate ions, a few of which are also illustrated in Fig. 28. It is also suggested that the various addition compounds, $(B_2O_3)_n,(SO_3)_m,(H_2O)_z$ reported by earlier workers can be rationalized in terms of polymeric ring structures of these types.

The use of solutions of boric acid in sulphuric acid as a means of analyzing organic materials, such as aldehydes, ketones, etc., by titration has been studied.[242] The complexes formed between boric acid and alizarin indicators in sulphuric acid solution have been studied,[243] and are suggested to be complexes with the tetra(hydrogensulphate) borate ion. Studies of the electrical conductivity of solutions in more concentrated oleums (65%) have indicated that an analogous pyrosulphatoborate ion, $B(HS_2O_7)_4^-$, is formed,[244] although boron trichloride was the reagent used to prepare the solution. However, further work with boric acid and boric oxide solutions[245] in 45% oleums has confirmed that these species can be formed directly.

Boron–sulphur–oxygen compounds are also referred to in Section A13.

H_3BO_3–H_3PO_4–H_2O. Much of the work with this system has been aimed at the eventual dehydration of reaction products to form boron phosphate, which is discussed elsewhere in this volume (Section A13). Levi and Gilbert[237] have examined portions of the system B_2O_3–P_2O_5–H_2O at 25°C. In addition to orthoboric acid, they obtained a solid phase with the composition BPO_4. Their results are illustrated in Fig. 29; compositions and solution densities are summarized in Table XL.

Englund has claimed[248] that when small amounts of water are added to a mixture of

Table XXXIX

Raman Spectra of Solutions of H_3BO_3, $HB(HSO_4)_4$, and $NaB(HSO_4)_4$ in H_2SO_4 (Frequencies in cm^{-1})

(*a*)		(*b*)	
396	H_2SO_4	393	H_2SO_4
422	H_2SO_4	412	H_2SO_4
564	H_2SO_4	563	H_2SO_4
588	HSO_4^-	—	—
—	—	—	—
—	—	—	—
—	—	730	$B(HSO_4)_4^-$
911	H_2SO_4	913	H_2SO_4
973	H_2SO_4	973	H_2SO_4
—		985	$H_3SO_4^+$
1040	HSO_4^-	—	—
1100	$B(HSO_4)_4^-$	1100	$B(HSO_4)_4^-$
1148	H_2SO_4	1140	H_2SO_4
1195	H_2SO_4,HSO_4^-	1195	H_2SO_4
1260	$B(HSO_4)_4^-$	1260	$B(HSO_4)_4^-$,$H_3SO_4^+$
1370	H_2SO_4	1365	H_2SO_4
—	—	1480	$H_3SO_4^+$

NOTE: (*a*) 0·4 molal H_3BO_3 in H_2SO_4; (*b*) 0·35 molal $HB(HSO_4)_4$ in H_2SO_4.

Raman Spectra of Concentrated Solutions of $HB(HSO_4)_4$ in H_2SO_4 (Frequencies in cm^{-1})

(*a*)	(*b*)	Assignment*
—	145 (2)	$H_2S_2O_7$
—	259 (1)	$H_2S_3O_{10}$
310 (4)	303 (6)	$H_2S_2O_7$
330 (6)	327 (10)	$H_2S_2O_7$
—	369 (1)	$H_2S_3O_{10}$
388 (2)	395 (1/2)	H_2SO_4
420 (2)	420 (2)	H_2SO_4
474 (1)	471 (3)	$H_2S_2O_7$
—	507 (4)	$H_2S_2O_7$
—	527 (3)	$H_2S_2O_7$
550 (10)	559 (2)	H_2SO_4
630 (1)	635 (1)	$H_2S_2O_7$,$B(HSO_4)_4^-$
661 (1/2−)	657 (1/2)	$B(HSO_4)_4^-$
703 (1)	702 (2)	$B(HSO_4)_4^-$
733 (4)	735 (6)	$H_2S_2O_7$,$B(HSO_4)_4^-$
805 (1/2)	802 (1)	$H_2S_2O_7$
909 (8)	906 (6)	H_2SO_4
970 (2)	966 (4)	H_2SO_4,$H_2S_2O_7$
985 (2)	983 (3)	$H_3SO_4^+$
—	1075 (1/2)	SO_3
1100 (3)	1100 (4)	$B(HSO_4)_4^-$
1140 (6)	1170 (6)	H_2SO_4
1210 (4)	1226 (8)	H_2SO_4,$H_2S_2O_7$
1265 (2)	1260 (2)	$H_3SO_4^+$,$B(HSO_4)_4^-$
1375 (2)	1360 (2)	H_2SO_4
1425 (1)	1421 (4)	$H_2S_2O_7$
1452 (1)	1461 (3)	$H_2S_3O_{10}$
1480 (1)	1480 (2)	$H_3SO_4^+$

NOTE: (*a*) 1·4 molal $HB(HSO_4)_4$ in H_2SO_4; (*b*) 5 molal $HB(HSO_4)_4$ in H_2SO_4.

* Many of the lines assigned to $H_2S_2O_7$ are probably common also to $H_2S_2O_{10}$ (1).

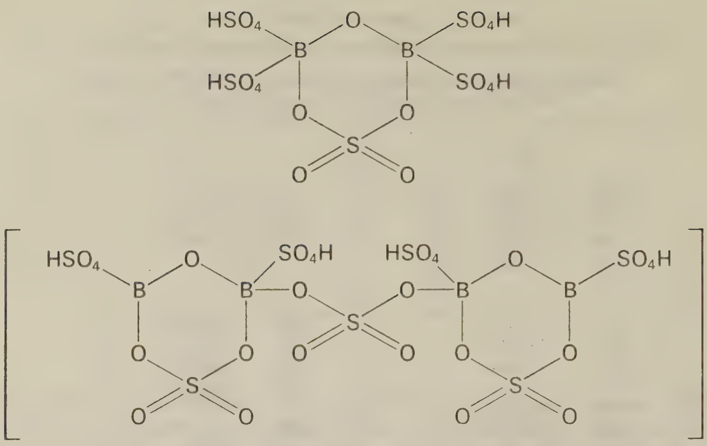


FIG. 28.—Polymeric hydrogen sulphate borate ions[241, 247]

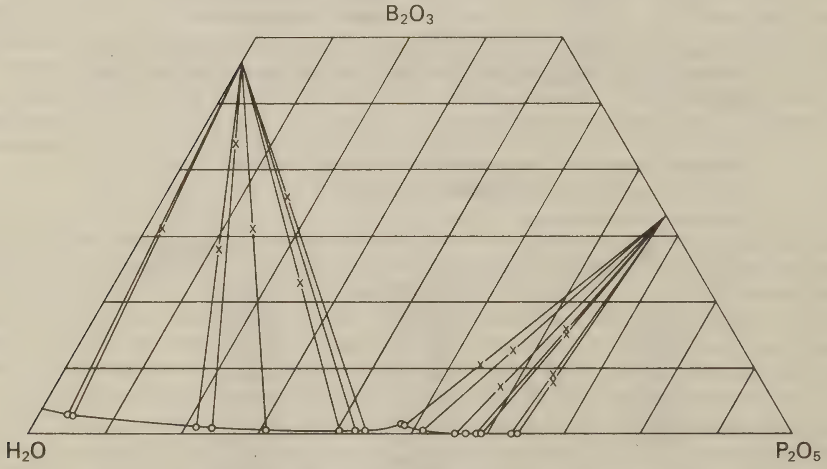


FIG. 29.—The system B_2O_3–P_2O_5–H_2O at 25°C[237]

boric acid and phosphorus pentoxide a novel acid, $B_4O_7(H_3P_2O_6)_2$ is formed as a dry powder; salts of this acid are claimed to be formed by adding the appropriate alkali to aqueous solutions of the acid. Johnstone[336] has claimed the use of this acid as a polymerization catalyst for olefins. Evidence for the formation of a 1:1 B–P mixed complex species in solution is claimed[249] from studies of the absorption of boron and phosphorus on ion-exchange resins from solutions containing boric and phosphoric acids.

H_3BO_3–HCl–H_2O. Earlier work on the effect of hydrochloric acid on the solubility of boric acid has been reviewed in Mellor.[82] It is claimed that metaboric acid can be used to prepare anhydrous hydrochloric acid from water solutions by volatilization of gaseous hydrogen chloride from mixtures.[250] The use of hydrochloric acid to prepare boric acid is discussed in the following section (A7). It is probably the volatility of hydrochloric acid from the solutions that has limited the study of the system.

H_3BO_3–CrO_3–H_2O. This system has been studied at 25°C.[251] Orthoboric acid appears to be the only boron-containing solid phase. The results are illustrated in

Table XL.—The System B_2O_3–P_2O_5–H_2O at 25°C[237]

$d_{4°}^{25°}$	Solutions Composition (g/100 g)		Wet solids Composition (g/100 g)		Solid phase
	P_2O_5	B_2O_3	P_2O_5	B_2O_3	
1·042	3·63	2·55	1·23	39·80	H_3BO_3
1·048	4·34	2·53	2·04	31·35	
1·190	21·51	1·12	11·09	27·91	
1·215	23·66	1·05	5·39	43·86	
1·281	31·01	0·62	14·10	31·03	
1·391	40·39	0·45	24·28	22·89	
	42·60	0·68	20·13	30·03	
1·434	43·70	0·68	16·11	35·78	
1·504	48·08	1·27	45·62	13·59*	
1·516	48·51	1·20			BPO_4
	48·89	1·11	54·43	10·49	
	51·52	0·23	57·81	12·70	
	55·37	concentration too low to be titrated	58·12	7·50	
	56·99				
	58·35		62·73	15·90	
1·645	58·68		62·81	15·02	
	62·81		64·06	8·95	
1·722	63·43		64·40	7·94	

* Apparently point of inversion.

Table XLI.—The System B_2O_3–CrO_3–H_2O[251]

Compositions (g/100 g) and densities at 25°C					Compositions (g/100 g) and densities at 45°C				
Liquid phase			Wet solid		Liquid phase			Wet solid	
$d_{4°}^{25°}$	CrO_3	B_2O_3	CrO_3	B_2O_3	$d_{4°}^{45°}$	CrO_3	B_2O_3	CrO_3	B_2O_3
1·699	62·40	0·10	32·38	26·09	1·674	61·56	0·90	39·31	20·84
1·657	59·90	0·16	35·82	22·36	1·612	58·10	0·92	33·96	23·91
	53·72	0·28			1·603	57·50	0·87	29·78	27·42
	49·75	0·42	45·39	5·28	1·603	57·34	1·12	32·71	24·43
1·420	43·80	0·65	24·42	24·89	1·528	53·80	0·85	24·28	29·88
	37·89	0·92	21·12	25·11	1·219	25·60	2·33	11·58	32·10
1·296	33·05	1·02	17·94	26·07	1·038	2·40	4·76	0·93	36·53
1·212	24·31	1·35	9·02	35·72					
1·156	18·07	1·58	9·30	28·52					
1·086	9·42	2·28	5·19	27·07					
1·052	4·90	2·79	2·50	31·01					

Fig. 30 and Table XLI. The buffering capacity of aqueous solutions containing $Cr_2(SO_4)_3$, H_3BO_3, Na_2SO_4, and NaF has been studied.[372]

Boric Acid—Inorganic Base Systems. These systems are described in Sections devoted to the metal borates. The highly important Na_2O–B_2O_3–H_2O system has been revised by Nies and Hulbert.[427]

General Effects of Added Salts on the Solubility of Boric Acid

Earlier studies of the effect of various salts on the solubility of orthoboric acid in water have been summarized in Mellor.[82] More recently Constable and Isnel [252, 253]

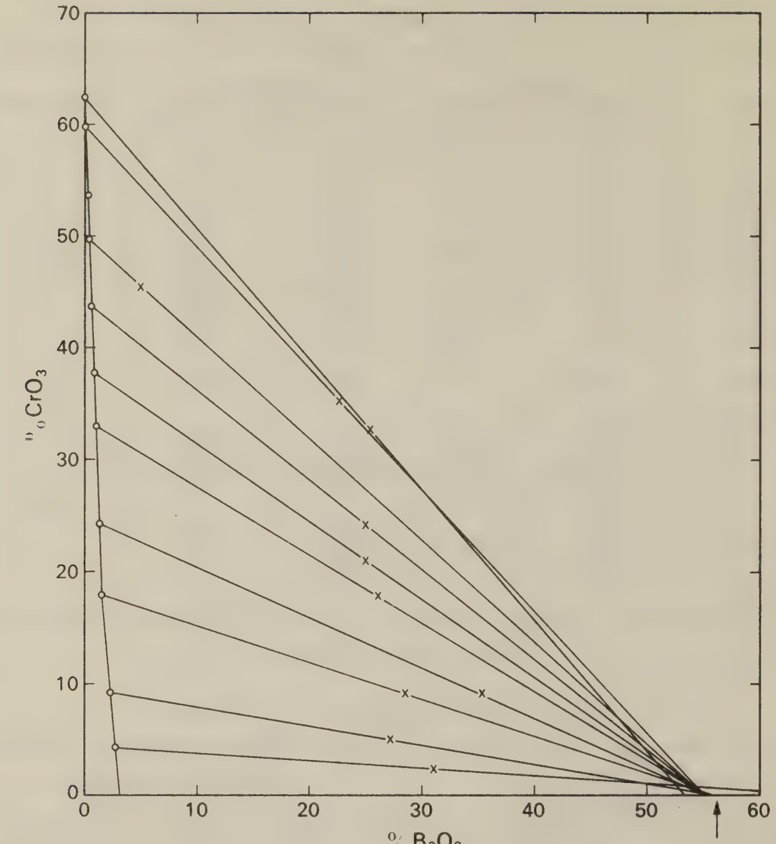


FIG. 30.—The solubility of boric acid in aqueous solutions of chromic acid at 25°C[251]

have examined the effect of added salt concentration and temperature on the solubility of orthoboric acid in water. They report that the data fit the general expression:

$$\log_{10} S = \log_{10} S_0 + K\sqrt{C}$$

where S is the solubility in g/100 g H_2O,
S_0 is the solubility in pure water, g/100 g H_2O,
K is an empirically determined constant characteristic of the particular salt added,
C is the concentration of added salt in g /100 g H_2O.

Table XLII and Fig. 30a summarize their results for S_0 and K covering temperatures from 0° to 100°C for a variety of added salts. In all the cases they studied, the solubility of boric acid increases with increasing concentration of added salt, increasing valence of the cation of the added salt, and decreasing ionization constant of the acids or bases from which the salts are derived. Similar results were obtained by Soldi at 0°C,[258] and are shown in Table XLIIa.

It is reported that dry mixtures of boric acids (either orthoboric acid or metaboric acids) react with alkali-metal[254–6] or ammonium[255] chlorides and nitrates when heated in a current of steam at temperatures of 100°C or higher to produce gaseous hydrochloric or nitric acid and the corresponding pentaborate; sodium salts, which apparently do not react completely, are an exception. Similar reactions are reported for alkaline-earth chlorides and nitrates starting at 150°C. The temperatures required for complete

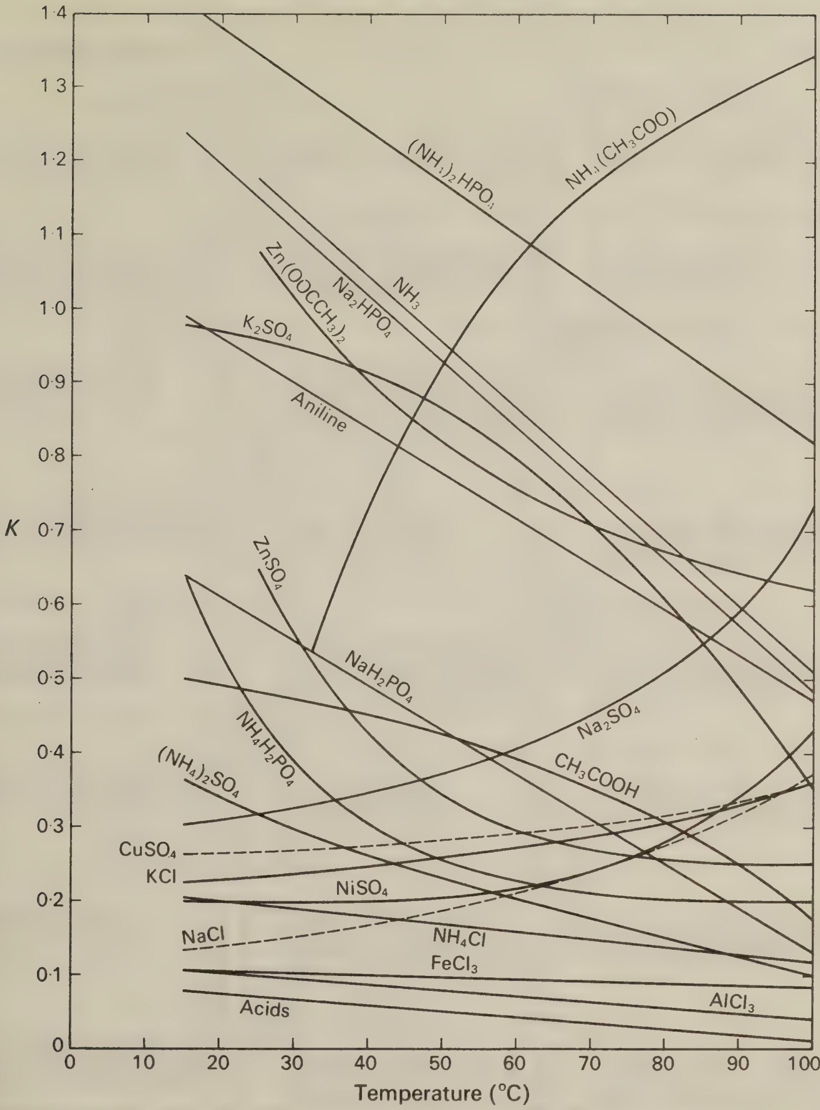


FIG. 30a.—Effect of added salts on boric acid solubility[253]

conversion into borate are summarized by Schalek and Koros,[256] who also claim a similar reaction for potassium sulphate.

Boric Acid–Inorganic Salt Systems

H_3BO_3–$NaNO_3$–H_2O. This system is claimed to show formation of a new compound in addition to the starting components, but its composition was not established.[294] The eutectic is at −18·5°C, with an equilibrium liquid-phase composition of 1·65% H_3BO_3, 37% $NaNO_3$, and 61·35% H_2O.

H_3BO_3–KNO_3–H_2O. This system shows no compound formation, only simple binary and ternary eutectics. The ternary eutectic is reported at either −3·2°C and 2·90%

*Table XLII.—Effect of Added Salts on Orthoboric Acid Solubility**[252]*

Temp.	NaCl		KCl		NH_4Cl		$NH_4(CH_3COO)$		Temp.
	log S_0 K (from graph)		log S_0 K (from graph)		log S_0 K (from graph)		log S_0 K (from graph)		
0	30103	0·0146	30103	0·230	30103	0·219	30103		0
10	43933	0·0152	43933	0·235	43933	0·210	43933		10
20	56820	0·0163	56820	0·240	56820	0·201	56820		20
30	69020	0·0174	69020	0·251	69020	0·195	69020		30
40	83885	0·0182	83885	0·259	83885	0·180	83885	0·70	40
50	94201	0·0198	94201	0·270	94201	0·172	94201	0·88	50
60	04532	0·0219	04532	0·290	04532	0·165	04532	1·01	60
70	14301	0·0237	14301	0·300	14301	0·160	14301	1·14	70
80	23019	0·0260	23019	0·320	23019	0·150	23019	1·22	80
90	35218	0·0285	35218	0·338	35218	0·141	35218	1·30	90
100	46835	0·0322	46835	0·370	46835	0·133	46835	1·34	100

Temp.	$(NH_4)_2SO_4$		$(NH_4)H_2PO_4$		$(NH_4)_2PO_4$		K_2SO_4		Temp.
	log S_0 K (from graph)		log S_0 K (from graph)		log S_0 K (from graph)		log S_0 K (from graph)		
0	30103	0·410	0·30103		0·30103		0·30103	1·00	0
10	43933	0·365	0·43933		0·43933		0·43933	0·971	10
20	56820	0·320	0·56820		0·56820		0·56820	0·938	20
30	69020	0·292	0·69020	0·380	0·69020	1·314	0·69020	0·901	30
40	83885	0·260	0·83885	0·302	0·83885	1·240	0·83885	0·850	40
50	94201	0·230	0·94201	0·269	0·94201	1·172	0·94201	0·800	50
60	04532	0·210	1·04532	0·242	1·04532	1·100	0·04532	0·710	60
70	14301	0·170	1·14301	0·220	1·14301	1·032	1·14301	0·610	70
80	23019	0·150	1·23019	0·213	1·23019	0·962	1·23019	0·475	80
90	35218	0·120	1·35218	0·210	1·35218	0·888	1·35218	0·350	90
100	46835	0·100	1·46835	0·201	1·46835	0·820	1·46835		100

Temp.	Na_2SO_4		$NaHCO_3$		Na_2CO_3		Na_2HPO_4		NaH_2PO_4		Temp.
	log S_0 K (from graph)		log S_0 K (from graph)		log S_0 K (from graph)		log S_0 K (from graph)		log S_0 K (from graph)		
0	0·30103	0·285	30103		30103		30103		0·30103		0
10	0·43933	0·300	43933		43933		43933		0·43933	0·659	10
20	0·56820	0·301	56820		56820	2·00	56820	1·192	0·56820	0·600	20
30	0·69020	0·303	69020	2·445	69020	1·882	69020	1·100	0·69020	0·544	30
40	0·83885	0·304	83885	2·294	83885	1·750	83885	1·023	0·83885	0·485	40
50	0·94201	0·307	94201	2·135	94201	1·623	94201	0·924	0·94201	0·428	50
60	1·04532	0·415	04532	1·970	04532	1·499	04532	0·842	1·04532	0·369	60
70	1·14301	0·465	14301	1·821	14301	1·374	14301	0·755	1·14301	0·310	70
80	1·23019	0·520	23019	1·663	23019	1·252	23019	0·663	1·23019	0·250	80
90	1·35218	0·590	35218	1·505	35218	1·112	35218	0·575	1·35218	0·188	90
100	1·46835	0·730	46835	1·361	46835	0·998	46835	0·489	1·46835	0·132	100

Table XLIIa.—Effect of Added Salts on Orthoboric Acid Solubility[258]

Solubility of H_3BO_3 on addition of CH_3COONa

CH_3COONa g %	$\sqrt{C}$	H_3BO_3 g %	log S
—	—	2·650	0·4232
2·05	1·432	3·005	0·4780
4·10	2·025	3·140	0·4970
8·20	2·870	3·400	0·5318

Solubility of H_3BO_3 on addition of C_6H_5COONa

C_6H_5COONa g %	$\sqrt{C}$	H_3BO_3 g %	log S
—	—	2·650	0·4232
2·5	1·581	2·930	0·4670
5	2·237	3·050	0·4840
7	2·583	3·140	0·4970

Solubility of H_3BO_3 on addition of $NaNO_2$

$NaNO_2$ g %	$\sqrt{C}$	H_3BO_3 g %	log S
—	—	2·650	0·4232
1·725	1·313	2·790	0·4456
3·450	1·857	2·875	0·4586
5·180	2·277	2·930	0·4668
6·900	2·627	2·960	0·4713

Solubility of H_3BO_3 on addition of $NaClO_2$

$NaClO_2$ g %	$\sqrt{C}$	H_3BO_3 g %	log S
—	—	2·65	0·4232
2	1·415	2·78	0·4450
3	1·732	2·83	0·4518
4	2·0	2·87	0·4578
5	2·236	2·89	0·4609
7	2·645	2·93	0·4660

Solubility of H_3BO_3 on addition of $CH_2BrCOONa$

$CH_2BrCOONa$ g %	$\sqrt{C}$	H_3BO_3 g %	log S
—	—	2·65	0·4232
3	1·733	2·78	0·4440
6	2·45	2·87	0·4570
9	3·00	2·90	0·4624

Solubility of H_3BO_3 on addition of $CH_2ClCOONa$

$CH_2ClCOONa$ g %	$\sqrt{C}$	H_3BO_3 g %	log S
—	—	2·65	0·4232
2·92	1·710	2·79	0·4456
5·85	2·416	2·85	0·4548
11·70	3·420	2·93	0·4668

Solubility of H_3BO_3 on addition of $HCOONa$

$HCOONa$ g %	$\sqrt{C}$	H_3BO_3 g %	log S
—	—	2·650	0·4232
1·7	1·304	2·855	0·4556
3·0	1·734	2·950	0·4698
5·0	2·237	3·020	0·4810
8·0	2·583	3·100	0·4913
9·0	3·0	3·150	0·4980

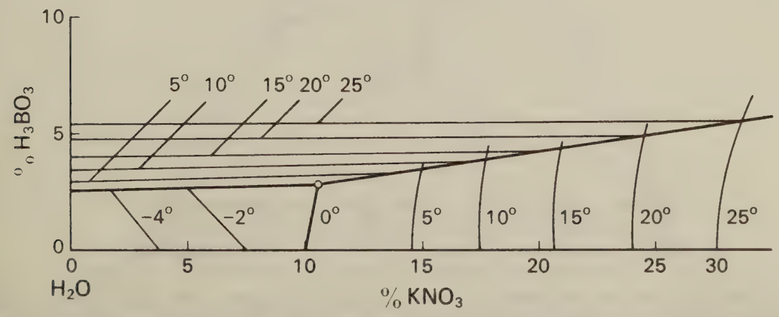


FIG. 31.—Solubility isotherms in the system H_3BO_3–KNO_3H_2O[259]

H_3BO_3, 10·75% KNO_3, 86·35% H_2O,[259] or −3·9°C and 3·4% H_3BO_3, 12·2% KNO_3, and 84·4% H_2O.[260] The results of Ugaĭ and Simkina[259] are illustrated in Fig. 31. They also calculated activity coefficients for boric acid in the solutions; these results, shown in Table XLIII, indicate a greater 'salting in' effect at lower temperature than at high temperature.

Table XLIII.—The System H_3BO_3–KNO_3–H_2O

Expt. No.	Composition of solution %			Composition of solution in moles per 1000 g H_2O			$1/m$	$\sqrt{\mu}$	λ H_3BO_3
	KNO_3	H_3BO_3	Σ	KNO_3	H_3BO_3	Σ			
				Temperature 0°C					
1	0·0	2·4	2·4	0·0	0·398	0·398	—	—	0·8890
2	3·89	2·7	6·59	0·412	0·468	0·880	2·139	0·938	0·7508
3	7·77	2·9	10·67	0·860	0·525	1·385	1·905	1·179	0·6686
4	10·67	3·0	13·67	1·223	0·559	1·782	1·790	1·338	0·6247
				Temperature 10°C					
1	0·0	3·5	3·5	0·0	0·587	0·587	—	—	0·8525
2	3·85	3·65	7·50	0·412	0·638	1·050	1·567	1·025	0·7836
3	7·70	3·75	11·45	0·860	0·685	1·545	1·460	1·245	0·7302
4	10·58	3·80	14·38	1·223	0·718	1·941	1·393	1·393	0·6968
5	13·45	3·90	17·35	1·610	0·763	2·373	1·311	1·540	0·6654
				Temperature 20°C					
1	0·0	4·75	4·75	0·0	0·807	0·807	—	—	0·8052
2	3·81	4·85	8·66	0·412	0·858	1·270	1·165	1·127	0·7565
3	7·60	4·95	12·55	0·860	0·916	1·776	1·092	1·261	0·7094
4	10·40	5·00	15·40	1·216	0·955	2·171	1·047	1·473	0·6795
5	13·30	5·00	18·30	1·611	0·990	2·601	1·010	1·613	0·6561

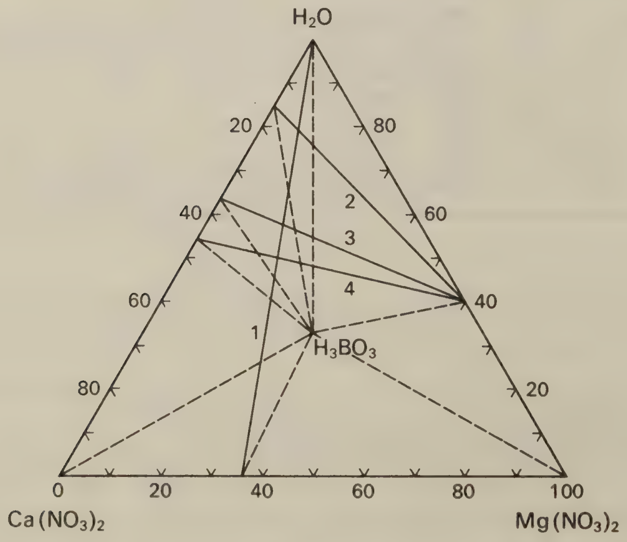


FIG. 32.—Diagram for the composition of the quaternary system. The sides of the triangle represent the contents of the components (in %); the numbers 1, 2, 3, 4 on the lines correspond to the numbers of the sections[262]

H_3BO_3–$Ca(NO_3)_2$–H_2O. The water solubility of the system $Ca(NO_3)_2$–H_3BO_3 has been determined at temperatures up to 90°C.[404, 408, 409] The study has practical relevance in the production of boric acid from colemanite.

H_3BO_3–$Ca(NO_3)_2$–$Mg(NO_3)_2$–H_2O. The data for the three ternary systems involved in the quaternary system were reported first,[263] followed by the data for the quaternary system[262] from 60°C to complete solidification. Four sections of the quaternary system were studied, all four of which pass through the boric acid vertex and intersect the

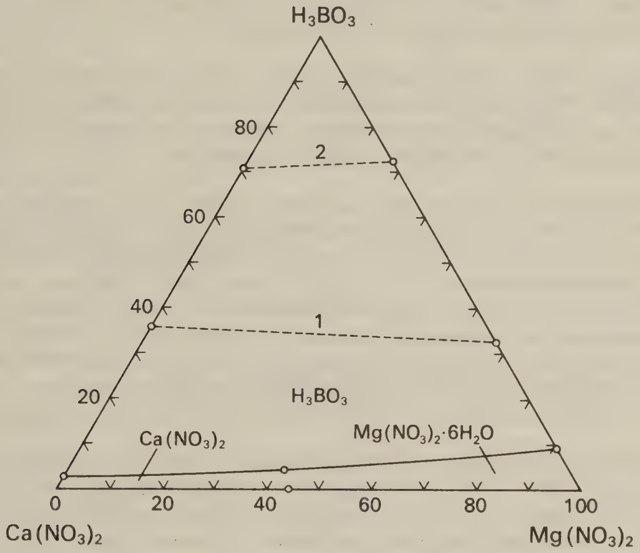


FIG. 33.[262] (a) Jänecke diagram for the isotherm at 0°C. Numbers on the broken lines represent the water content (in g): (1) 250; (2) 500; (3) 1000; (4) 2000; (5) 3000

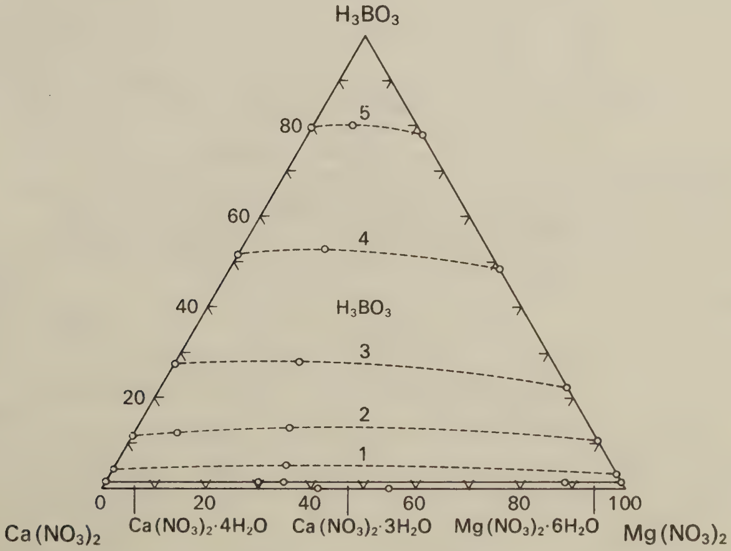


FIG. 33.[262] (b) Jänecke diagram for the isotherm at 60°C. Numbers on the broken lines represent the water content (in g): (1) 250; (2) 500

other sides, as illustrated in Fig. 32. Boric acid occupies nearly all the crystalline volume of the system, as its solubility is far less than that of the nitrates, as illustrated by the Jänecke diagrams for 0°C and 60°C, shown in Fig. 33a, b. The minimum solubility of boric acid (less than 0·25%) occurs at the quaternary eutectic. Boric acid is more soluble in mixtures containing more magnesium nitrate. Between 20°C and complete solidification there are six areas of crystallization, meeting in three points; they are (1) a eutectic at −35·8°C with 23·0% $Mg(NO_3)_2$, 17·4% $Ca(NO_3)_2,4H_2O$, and 0·25% H_3BO_3, and (2) two transition points at −21°C and −7·1°C, the first in the fields $Mg(NO_3)_2,9H_2O$, $Ca(NO_3)_2,4H_2O$, H_3BO_3, and $Mg(NO_3)_2,6H_2O$, and the second in the fields of $Mg(NO_3)_2,9H_2O$, $Ca(NO_3)_2,4H_2O$, H_3BO_3, and $Ca(NO_3)_2,3H_2O$. There is no evidence for formation of solid complex borates in this system.

H_3BO_3–$(NH_4)_2SO_4$–H_2O. The solubility of B_2O_3 in the system HBO_2–$(NH_4)_2SO_4$–H_2O was studied.[448] In dilute solutions orthoboric acid is formed, its solubility increasing with the $(NH_4)_2SO_4$ concentration, whereas the solubility of ammonium sulphate decreases with increasing boric acid concentration.

H_3BO_3–Na_2SO_4–H_2O. This system has been studied by a number of investigators[264–6, 292]; the earlier data are summarized in Mellor.[82] Teeple[265] reported the eutonic points on the 20·5°, 23·5°, 28·5°, and 35°C isotherms. Palkin and Goloshchapov[264] investigated the system at 0°, 10°, 20°, 25°, and 29·8°C. Bekturov and Litvinenko[266] studied the system at 15°C, and Konobritskii at 5°C. The solubility of each component is increased in the presence of the other, and there are no complex compounds formed, which is further confirmed by cryoscopic studies of boric acid dissolved in Glauber's salt ($Na_2SO_4,10H_2O$).[267] The eutectic is reported to occur at −1·6°C, with an equilibrium liquid composition of 2·5% H_3BO_3, 3·8% Na_2SO_4, and 9·37% H_2O.[292]

H_3BO_3–Na_2SO_4–$Na_2B_4O_7$–H_2O. This quaternary system is reported by Teeple[265] at temperatures of 20·5°, 23·5°, 28·5° and 35°C. A typical isotherm (at 35°C) is illustrated in Fig. 34. Compositions of the invariant points are summarized in Table XLIV. This system has considerable practical significance, industrial production of boric acid

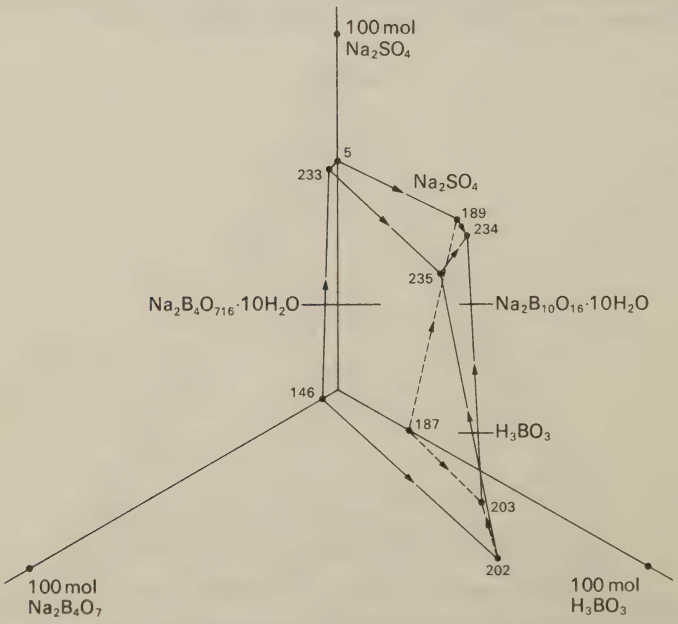


FIG. 34.—System Na_2SO_4–$Na_2B_4O_7$–H_3BO_3–H_2O at 35°C[265]

Table XLIV.—Invariant Points in the System H_3BO_3–Na_2SO_4–$Na_2B_4O_7$–H_2O[265]

20·5°C

Point	Solid phases	g/100 g H_2O				Mol/1000 mol H_2O			
		H_3BO_3	$Na_2B_4O_7$	Na_2SO_4	Total	H_3BO_3	$Na_2B_4O_7$	Na_2SO_4	Total
206	$Na_2B_4O_7.10H_2O$	—	2·5	—	2·5	—	2·2	—	2·2
207	H_3BO_3	4·9	—	—	4·9	14·3	—	—	14·3
208	$Na_2SO_4.10H_2O$	—	—	20·2	20·2	—	—	25·7	25·7
209	$Na_2B_4O_7.10H_2O$, $Na_2SO_4.10H_2O$	—	1·2	20·0	21·2	—	1·0	25·4	26·4
210	H_3BO_3,$Na_2SO_4.10H_2O$	7·6	—	25·3	32·9	22·1	—	32·0	54·1
211	H_3BO_3, $Na_2B_{10}O_{16}\cdot10H_2O$	11·5	5·8	—	17·3	33·3	5·2	—	38·5
212	$Na_2B_4O_7.10H_2O$, $Na_2B_{10}O_{16}\cdot10H_2O$	12·0	8·7	—	20·7	34·8	7·7	—	42·5
213	$Na_2SO_4.10H_2O$,H_3BO_3, $Na_2B_{10}O_{16}\cdot10H_2O$	9·8	1·9	25·8	37·5	28·3	1·7	32·6	62·6
214	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$, $Na_2B_{10}O_{16}\cdot10H_2O$	8·8	4·7	23·6	37·1	25·5	4·2	29·9	59·6

23·5°C

Point	Solid phases	g/100 g H_2O				Mol/1000 mol H_2O			
		H_3BO_3	$Na_2B_4O_7$	Na_2SO_4	Total	H_3BO_3	$Na_2B_4O_7$	Na_2SO_4	Total
215	$Na_2B_4O_7.10H_2O$	—	2·9	—	2·9	—	2·6	—	2·6
216	H_3B_3O	5·5	—	—	5·5	16·0	—	—	16·0
217	$Na_2SO_4.10H_2O$	—	—	25·2	25·2	—	—	32·0	32·0
218	$Na_2B_4O_7.10H_2O$, $Na_2SO_4.10H_2O$	—	1·4	23·7	25·1	—	1·2	30·1	31·3
219	H_3BO_3, $Na_2SO_4.10H_2O$	8·9		31·2	40·1	25·9	—	39·5	65·4
220	H_3BO_3, $Na_2B_{10}O_{16}\cdot10H_2O$	12·6	6·2	—	18·8	36·7	5·6	—	42·3
221	$Na_2B_4O_7.10H_2O$, $Na_2B_{10}O_{16}\cdot10H_2O$	13·2	10·4	—	23·6	38·4	9·3	—	47·7
222	$Na_2SO_4.10H_2O$,H_3BO_3, $Na_2B_{10}O_{16}\cdot10H_2O$	10·9	1·9	31·3	44·1	31·7	1·7	39·6	73·0
223	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$ $Na_2B_{10}O_{16}\cdot10H_2O$	9·6	5·4	28·3	43·3	27·8	4·8	35·9	68·5

28·5°C

Point	Solid phases	g/100 g H_2O				Mol/1000 mol H_2O			
		H_3BO_3	$Na_2B_4O_7$	Na_2SO_4	Total	H_3BO_3	$Na_2B_4O_7$	Na_2SO_4	Total
224	$Na_2B_4O_7.10H_2O$	—	3·7	—	3·7	—	3·3	—	3·3
225	H_3BO_3	6·3	—	—	6·3	18·4	—	—	18·4
226	$Na_2SO_4.10H_2O$	—	—	36·5	36·5	—	—	46·2	46·2
227	$Na_2B_4O_7.10H_2O$, $Na_2SO_4.10H_2O$	—	1·7	36·1	37·8	—	1·5	45·8	47·3
228	H_3BO_3, $Na_2SO_4.10H_2O$	10·6	—	47·3	57·9	30·9	—	59·9	90·8
229	H_3BO_3, $Na_2B_{10}O_{16}\cdot10H_2O$	14·9	7·0	—	21·9	43·2	6·3	—	49·5
230	$Na_2B_4O_7.10H_2O$, $Na_2B_{10}O_{16}\cdot10H_2O$	16·2	13·4	—	29·6	47·0	12·0	—	59·0
231	$Na_2SO_4.10H_2O$,H_3BO_3, $Na_2B_{10}O_{16}\cdot10H_2O$	12·1	1·7	47·8	61·6	35·3	1·5	60·6	97·4
232	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$, $Na_2B_{10}O_{16}\cdot10H_2O$	10·6	7·1	43·1	60·8	30·7	6·4	54·6	91·7

Table XLVI.—continued

35°C

Point	Solid phases	g/100 g H_2O				Mol/1000 mol H_2O			
		H_3BO_3	$Na_2B_4O_7$	Na_2SO_4	Total	H_3BO_3	$Na_2B_4O_7$	Na_2SO_4	Total
146	$Na_2B_4O_7.10H_2O$	—	5·3	—	5·3	—	4·7	—	4·7
187	H_3BO_3	7·9	—	—	7·9	22·8	—	—	22·8
5	Na_2SO_4	—	—	50·7	50·7	—	—	64·2	64·2
233	$Na_2B_4O_7.10H_2O$, Na_2SO_4	—	2·7	49·7	52·4	—	2·4	62·9	65·3
189	H_3BO_3,Na_2SO_4	13·1	—	53·0	66·1	38·1	—	67·1	105·2
203	H_3BO_3, $Na_2B_{10}O_{16}.10H_2O$	18·4	8·4	—	26·8	53·5	7·5	—	61·0
202	$Na_2B_4O_7.10H_2O$, $Na_2B_{10}O_{16}.10H_2O$	24·7	23·6	—	48·3	71·6	21·0	—	92·6
234	Na_2SO_4,H_3BO_3, $Na_2B_{10}O_{16}.10H_2O$	14·9	2·3	52·1	69·3	43·2	2·1	66·0	111·3
235	Na_2SO_4, $Na_2B_4O_7.10H_2O$, $Na_2B_{10}O_{16}.10H_2O$	15·2	12·4	47·0	74·6	44·0	11·1	59·6	114·7

in the United States being by the reaction of borax with sulphuric acid to give sodium sulphate as by-product.

H_3BO_3–$MgSO_4$–H_2O. This system has been studied over the temperature range 0–90°C.[268, 269] The study is complicated by the tendency for magnesium sulphate hexahydrate to form supersaturated solutions with relatively long periods of existence. The data for the system are illustrated in Fig. 35, taken from Manole–Bezhan.[268] The polytherm consists of two branches; the one from 10°–48°C is the curve for boric acid and magnesium sulphate heptahydrate; the one from 48°–80°C is for boric acid and magnesium sulphate hexahydrate.

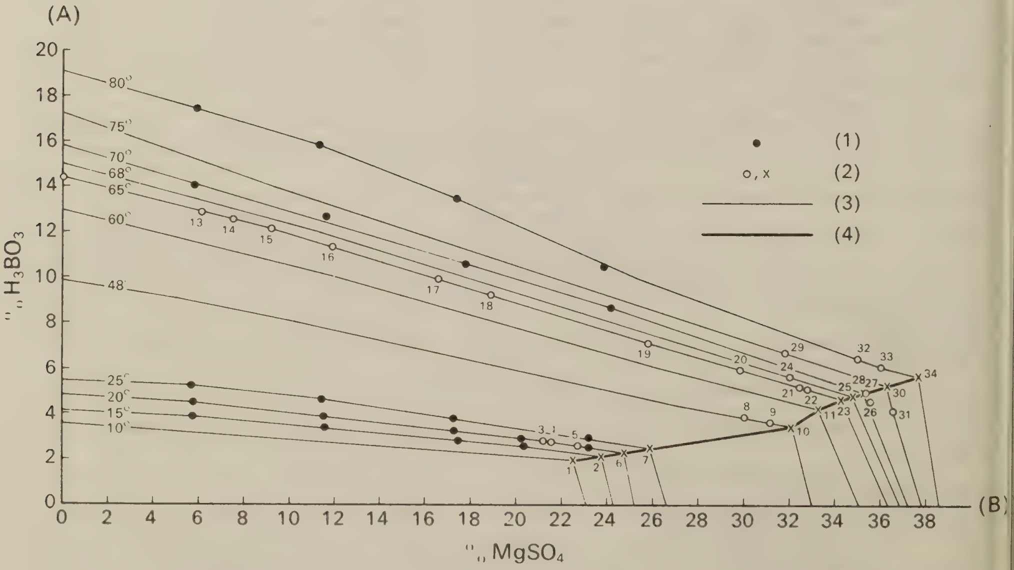


FIG. 35.—Experimental points on solubility isotherms and polytherm for the system H_3BO_3–$MgSO_4$–H_2O.[268] (A) H_3BO_3 (%), (B) $MgSO_4$ (%). (1) L. E. Berlin's data; (2) author's data; (3) isotherms; (4) polytherm

Refs. p. 311

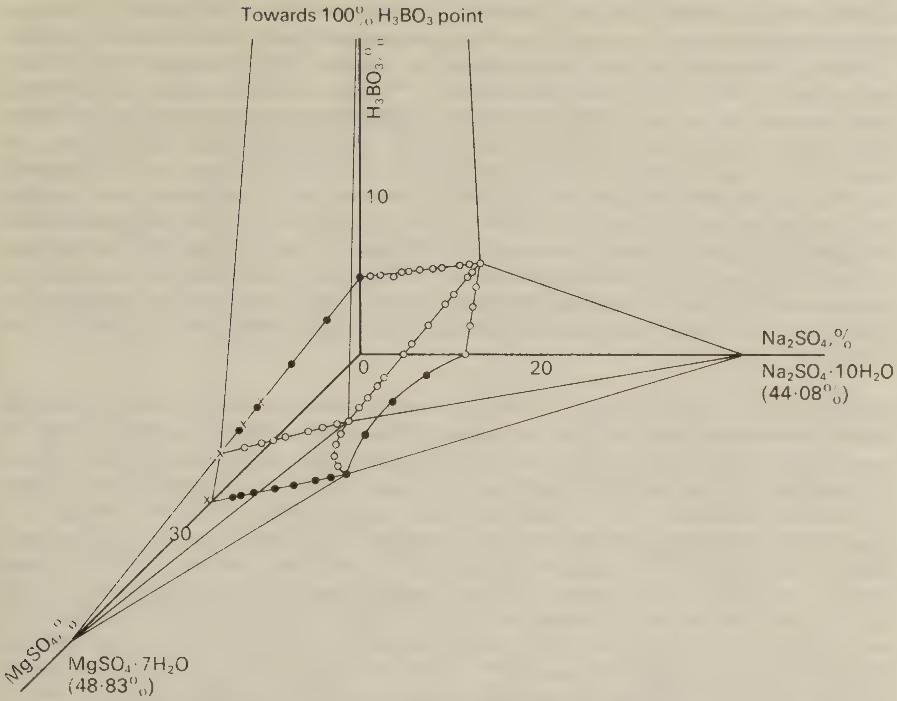


FIG. 36.—Solubilities in the H_3BO_3–$MgSO_4$–Na_2SO_4–H_2O system at 15°C[266]

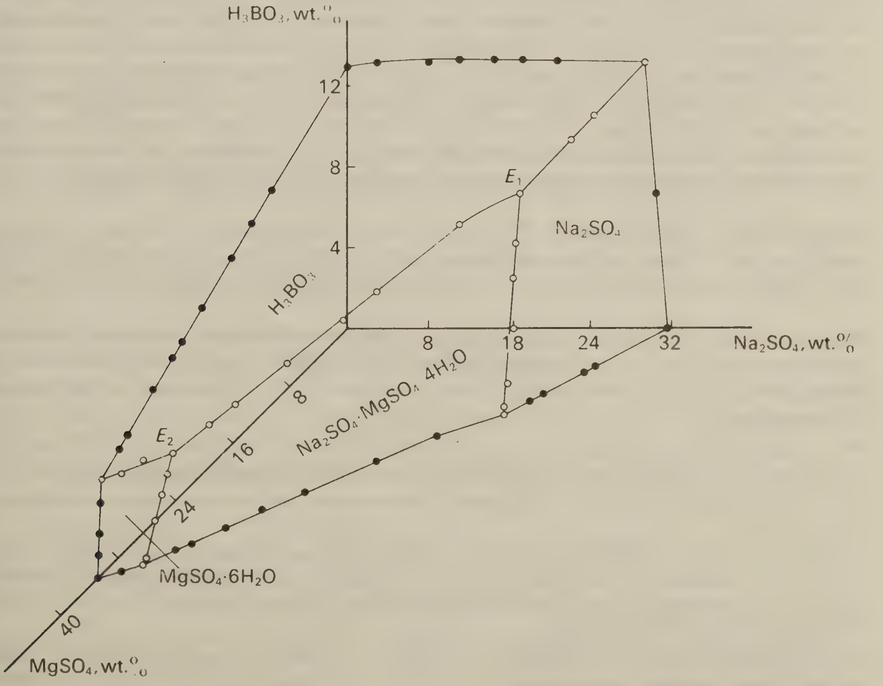


FIG. 37.—Isotherm of mutual solubility in the H_3BO_3–Na_2SO_4–$MgSO_4$–H_2O system at 60°C[272]

H_3BO_3–Na_2SO_4–$MgSO_4$–H_2O. Because of its application to the recovery of borate values from the naturally occurring calcium magnesium and calcium sodium borates in Russia, this system has received considerable attention.[266, 270–4] Isotherms have been studied at 5°C,[274] 35°C,[270] 50°C,[271] and 60°C.[272] Boric acid occurs as an equilibrium solid phase at all temperatures studied. At lower temperatures magnesium sulphate heptahydrate and sodium sulphate decahydrate occur as the other solid phases, as illustrated in Fig. 36, showing the isotherm at 15°C.[266] As the temperature is increased to 35°C, astrakanite ($Na_2SO_4,MgSO_4,4H_2O$) appears as an additional solid phase, and anhydrous sodium sulphate rather than Glauber's salt is formed; magnesium sulphate heptahydrate is still present. At 50°C the only further change is the appearance of magnesium sulphate hexahydrate instead of the heptahydrate; the same phases are present at 60°C. Fig. 37 illustrates the system at 60°C. The three invariant points in the system and corresponding concentrations in the liquid phase are summarized in Table XLV.

H_3BO_3–H_2SO_4–$MgSO_4$–H_2O. This system is also of interest in the recovery of borate values from natural minerals, and consequently has been studied a number of times in the temperature range 0–50°C. A method of analyzing the equilibrium brines by conductometric titration has been described.[277] The solubility of boric acid in the system is relatively insensitive to the sulphuric acid concentration, but the solubility of magnesium sulphate is decreased by the presence of sulphuric acid at temperatures from 35° to 65°C.[276] The minimum solubility of boric acid at 0°C is 0·92%, with 21·55% and 10·28% of sulphuric acid and magnesium sulphate, respectively.[279] At 0°C the equilibrium solid phases are: $MgSO_4,7H_2O$, $MgSO_4,6H_2O$, $MgSO_4,4H_2O$, and H_3BO_3; at 50°C they are $MgSO_4,6H_2O$, $MgSO_4,5H_2O$, $MgSO_4,H_2O$, and H_3BO_3. The data of Scholle and Machacova[281] at 25°, 55°, and 65°C are shown in Tables XLVa and XLVb. Treiman subsequently determined solubilities in the system at 25° and 75°C.[405, 406]

H_3BO_3–K_2SO_4–H_2O. This system has been studied from −2° to 100°C over a period of years by Perova.[282–4] It is a simple eutectic system with the three starting components as the only equilibrium phases. The eutectic is at −2°C, with a liquid-phase composition of 3·1% H_3BO_3, 6·6% K_2SO_4, and 90·7% H_2O. Figure 38 illustrates the data obtained. The electrical conductivity and viscosity of the solutions have been studied; the results are summarized in Tables XLVI and XLVII; they show that the viscosity of potassium sulphate solutions increases with increasing boric acid concentration, and it is postulated that the corresponding decrease in electrical conductivity is due to the increased viscosity.

H_3BO_3–K_2SO_4–$MgSO_4$–H_2O. The system was studied from 25°C down to complete solidification.[285] There are four equilibrium solid phases, H_3BO_3, K_2SO_4, $MgSO_4,6H_2O$, and $MgSO_4,12H_2O$ at 0°C; at 15°C and 25°C, $MgSO_4,7H_2O$ replaces $MgSO_4,12H_2O$.

H_3BO_3–K_2SO_4–KCl–H_2O. This system is reported by Teeple[265]; the 35°C isotherm is illustrated in Fig. 39, and summarized in Table XLVIII. The only equilibrium solid phases are the starting components. The solubility of all are increased in the presence of the others.

Table XLV.—Invariant Points in the System H_3BO_3–Na_2SO_4–$MgSO_4$–H_2O[273]

Reaction	Temp. °C	Wt. % in liquid		
		H_3BO_3	Na_2SO_4	$MgSO_4$
$Na_2SO_4.10H_2O + MgSO_4.7H_2O \rightarrow Na_2SO_4.MgSO_4.4H_2O + 13H_2O$	23·4	2·91	13·7	19·75
$Na_2SO_4.10H_2O \rightarrow Na_2SO_4 + 10H_2O$	27·0	4·55	24·0	8·80
$MgSO_4.7H_2O \rightarrow MgSO_4.6H_2O + H_2O$	44·4	3·52	6·9	27·59

Table XLVa.—System H_2SO_4–$MgSO_4$–H_3BO_3–H_2O at 25°C[281]

Equilibrium	Saturated solution % by weight			Wet residue % by weight			Solid phase
	H_2SO_4	$MgSO_4$	H_3BO_3	H_2SO_4	$MgSO_4$	H_3BO_3	
Hours							
4	3·21	23·24	2·24	0·37	33·77	25·68	$MgSO_4.7H_2O + H_3BO_3$
4	3·99	22·94	2·37	0·31	40·50	12·78	$MgSO_4.7H_2O + H_3BO_3$
4	6·47	22·25	2·13	—	—	—	$MgSO_4.7H_2O + H_3BO_3$
4	8·15	21·11	2·01	0·76	39·72	12·11	$MgSO_4.7H_2O + H_3BO_3$
4	10·78	20·91	1·93	—	—	—	$MgSO_4.7H_2O + H_3BO_3$
4	15·17	21·93	1·61	1·01	40·41	11·13	$MgSO_4.7H_2O + H_3BO_3$
4	18·01	18·55	1·54	1·32	39·52	15·88	$MgSO_4.7H_2O + H_3BO_3$
4	28·39	20·38	1·13	5·05	33·60	28·98	$MgSO_4.5H_2O + H_3BO_3$[a]
4	29·30	20·47	1·09	—	—	—	$MgSO_4.5H_2O + H_3BO_3$[a]
4	36·49	20·16	1·01	4·86	36·95	29·59	$MgSO_4.5H_2O + H_3BO_3$[a]
4	37·76	20·07	1·10	10·01	25·30	39·87	$MgSO_4.5H_2O + H_3BO_3$[a]
20	55·52	2·15	1·68	43·60	11·93	14·01	$MgSO_4.H_2O + H_3BO_3$
20	55·88	2·43	1·69	42·29	15·63	10·36	$MgSO_4.H_2O + H_3BO_3$
20	58·18	1·66	1·71	36·57	24·79	10·32	$MgSO_4.H_2O + H_3BO_3$
4	63·59	0·42	22·68	42·28	27·17	19·28	$3MgSO_4.2H_2SO_4.3{\cdot}5H_2O + 2H_3BO_3.H_2SO_4$
4	64·62	0·63	20·03	46·94	29·93	8·94	$3MgSO_4.2H_2SO_4,3{\cdot}5H_2O$[b]
4	66·34	0·47	12·94	44·86	31·12	10·15	$3MgSO_4.2H_2SO_4.3{\cdot}5H_2O + H_3BO_3$
4	67·20	1·42	5·28	43·99	30·10	11·94	$3MgSO_4.2H_2SO_4.3{\cdot}5H_2O + H_3BO_3$
Days							
7	9·95	20·68	1·62	—	—	—	$MgSO_4.7H_2O + H_3BO_3$
7	25·24	18·86	2·31	—	—	—	$MgSO_4.7H_2O + H_3BO_3$
7	27·78	20·04	1·25	—	—	—	$MgSO_4.6H_2O + H_3BO_3$
7	31·13	18·80	1·09	—	—	—	$MgSO_4.5H_2O + H_3BO_3$[a]
30	32·80	14·60	1·44	—	—	—	$MgSO_4.H_2O + H_3BO_3$
14	36·03	9·84	3·30	18·21	46·02	6·82	$MgSO_4.H_2O + H_3BO_3$
14	41·12	6·05	1·59	18·50	44·23	7·24	$MgSO_4.H_2O + H_3BO_3$
30	43·25	7·37	1·06	—	—	—	$MgSO_4.H_2O + H_3BO_3$
15	46·17	0·78	1·55	23·55	23·03	27·82	$MgSO_4.H_2O + H_3BO_3$
15	51·99	1·32	1·33	—	—	—	$MgSO_4.H_2O + H_3BO_3$
15	56·48	0·51	15·40	31·16	21·64	26·83	$MgSO_4.H_2O + H_3BO_3$
15	57·32	0·21	26·42	51·25	7·78	22·91	$MgSO_4.H_2O$[b]
30	58·79	1·14	1·45	—	—	—	$MgSO_4.H_2O + H_3BO_3$
30	61·39	1·00	1·77	18·72	43·92	12·57	$MgSO_4.H_2O + H_3BO_3$
30	62·56	0·69	2·06	—	—	—	$MgSO_4.H_2O + H_3BO_3$
15	59·60	0·20	19·52	54·49	4·56	22·22	$MgSO_4.H_2O + 2H_3BO_3.H_2SO_4$
30	63·35	0·23	26·82	—	—	—	
30	65·16	0·89	14·85	—	—	—	
7	65·18	0·24	27·61	—	—	—	
33	67·33	0·62	3·42	—	—	—	

[a] Unstable system. [b] Not saturated with H_3BO_3.

H_3BO_3–Na_2SO_4–NaCl–H_2O. This system is reported at 35° and 75°C by Teeple.[265] The results are summarized in Table XLIX and Fig. 40. Again the components are the only solid equilibrium phases, and the solubility of each is increased in the presence of the others.

H_3BO_3–NaCl–$Na_2B_4O_7$–H_2O. This system is reported at 35°C by Teeple,[265] and the data are presented in Fig. 41 and Table L. In this system there is another equilibrium solid phase, sodium pentaborate, in addition to the starting components.

H_3BO_3–KCl–$K_2B_{10}O_{16}$,$8H_2O$–H_2O. Teeple[265] has reported on this system at 35°C. It is similar to the preceding system, except that the tetraborate was not included. The results are shown in Fig. 42 and Table LI.

Table XLVb.—System H_2SO_4–$MgSO_4$–H_3BO_3–H_2O at 55°C and 65°C[281]

Equilibrium hours	Saturated solution % by weight			Wet residue % by weight			Solid phase
	H_2SO_4	$MgSO_4$	H_3BO_3	H_2SO_4	$MgSO_4$	H_3BO_3	
4	20·22	26·16	2·50	12·84	36·56	16·59	$MgSO_4.H_2O+H_3BO_3$
4	33·19	17·24	1·65	—	—	—	$MgSO_4.H_2O+H_3BO_3$[a]
4	44·02	8·26	2·48	—	—	—	$MgSO_4.H_2O+H_3BO_3$[a]
4	60·14	2·15	3·37	—	—	—	$MgSO_4.H_2O+H_3BO_3$[a]
4	60·64	1·15	22·94	43·18	24·96	15·31	$MgSO_4.H_2O$[b]
4	60·87	1·42	18·87	34·61	17·98	26·70	$MgSO_4.H_2O+H_3BO_3$
4	63·42	1·96	11·14	27·35	30·10	19·73	$MgSO_4.H_2O+H_3BO_3$

[a] Interpolated. [b] Not saturated with H_3BO_3.

Equilibrium hours	Saturated solution % by weight			Wet residue % by weight			Solid phase
	H_2SO_4	$MgSO_4$	H_3BO_3	H_2SO_4	$MgSO_4$	H_3BO_3	
4	23·80	20·19	3·28	—	—	—	$MgSO_4.H_2O+H_3BO_3$
4	38·55	12·82	3·53	—	—	—	$MgSO_4.H_2O+H_3BO_3$
4	42·60	8·10	3·27	—	—	—	$MgSO_4.H_2O+H_3BO_3$
4	46·50	6·57	3·22	24·33	30·20	19·04	$MgSO_4.H_2O+H_3BO_3$
4	47·07	4·68	3·24	29·65	29·08	8·24	$MgSO_4.H_2O+H_3BO_3$
4	50·23	4·70	3·43	—	—	—	$MgSO_4.H_2O+H_3BO_3$
4	52·14	4·63	3·75	—	—	—	$MgSO_4.H_2O+H_3BO_3$
4	52·91	3·79	3·30	—	—	—	$MgSO_4.H_2O+H_3BO_3$
4	54·58	2·62	5·47	35·69	17·96	19·09	$MgSO_4.H_2O+H_3BO_3$
4	54·98	2·57	3·89	—	—	—	$MgSO_4.H_2O+H_3BO_3$
4	61·43	1·53	17·56	34·65	39·65	8·65	$MgSO_4.H_2O$[a]
4	62·23	1·55	8·29	18·44	20·39	55·50	$MgSO_4.H_2O+H_3BO_3$
4	70·72	1·86	22·69	28·57	6·84	38·73	

[a] Not saturated with H_3BO_3.

Table XLVI.—Results of Measuring Electrical Conductivity of Potassium Sulphate Solutions[284]

Quantity of H_3BO_3 (wt. %)	Specific electrical conductivity of aqueous K_2SO_4 solutions containing the indicated %: $(\Omega^{-1}\cdot cm^2\cdot 10^4)$							
	2		4		6		10	
	At temperature (°C)							
	25	50	25	50	25	50	25	50
—	240	360	445	684	637	818	1005	1146
1.0	223	385	422	—	594	791	931	1117
2·0	217	323	400	569	562	774	883	1005
3·0	213	—	384	—	537	754	848	1072
4·0	211	309	373	541	517	740	820	1053
5·0	288	—	361	527·5	503	727	810	1034
6·0	Crystallized	291	Crystallized	512	492	717	796	1016
7·0		—		498	Crystallized	702	Crystallized	1003
8·0		279		484·2		700		987
9·0		262	—	—	—	—	—	—
10·0	—	—	Crystallized	469	—	—	—	—

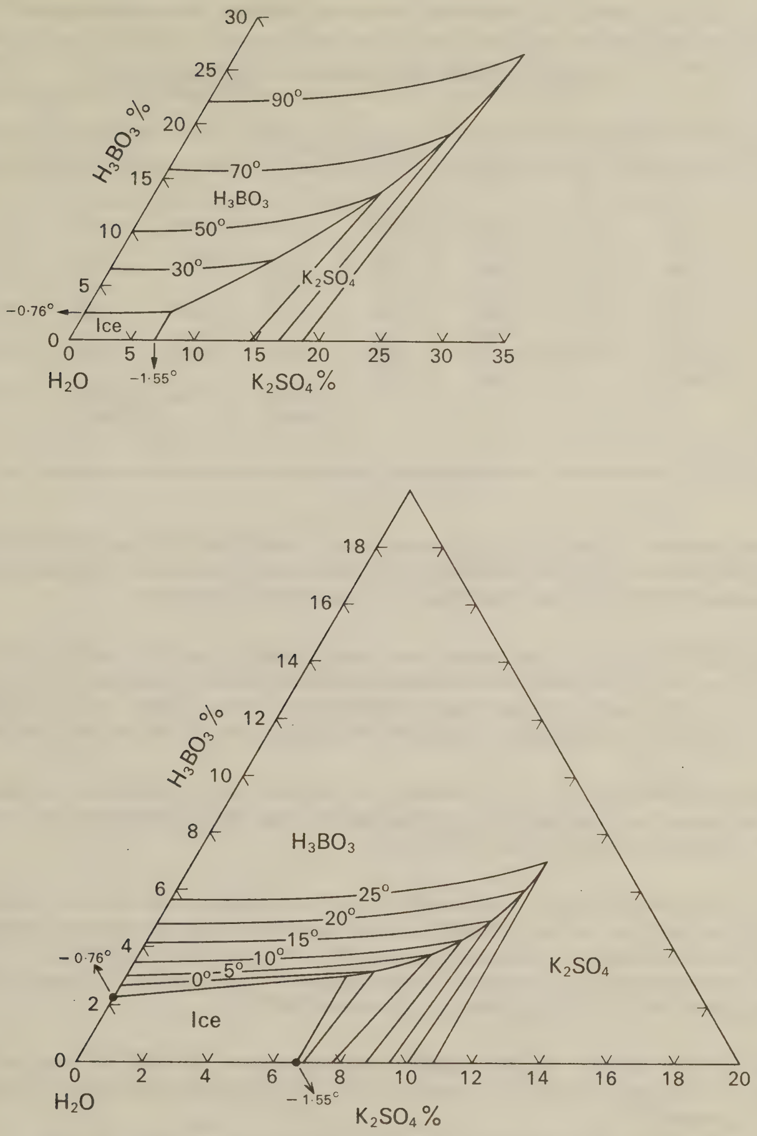


FIG. 38.—The system H_3BO_3–K_2SO_4–H_2O (compositions in wt %)[283, 282]

H_3BO_3–NaH_2PO_4–H_2O. Various kinds of reaction products were obtained on dehydration of mixtures of $NaH_2PO_4,2H_2O$ and H_3BO_3 with various mole ratios by heating at 400° ~ 750°C.[429] When a mixture of 3 moles of $NaH_2PO_4,2H_2O$ and 2 moles of H_3BO_3 was heated at 400° ~ 600°C, a new compound containing macromolecular chains with a skeleton of B–O–P linkages was considered to be formed; the obtained compound was a light, finely-divided and sparingly soluble powder and its melting point was about 700°C. When initial mixtures had a mole ratio of $NaH_2PO_4,2H_2O$ to H_3BO_3 other than that of 3:2, the reaction products consisted of some complicated polymers characterized by the formation of B–O–P linkages. In the cases of the glassy products with n value of 9 ~ 18, their water-soluble parts showed the ortho-:pyro-: tri-:high polymeric phosphoric acid ratio (in P_2O_5) to be 1:4:2:2 ($n = 6$); here, n refers

Table XLVII.—Results of Measuring Potassium Sulphate Solution Viscosities[284]

Quantity of H_3BO_3 (wt. %)	Viscosity (c-poises·10) of aqueous K_2SO_4 solutions (%):							
	2		4		6		10	
	At temperature (°C)							
	25	50	25	50	25	50	25	50
—	8·26	5·432	8·362	5·568	8·487	5·682	8·829	5·94
1·0	8·33	—	8·41	—	—	—	—	—
2·0	8·40	5·519	8·49	5·593	8·654	5·74	8·921	6·152
3·0	8·49	—	8·585	—	—	—	—	—
4·0	8·61	5·731	8·69	5·685	8·943	5·845	9·293	6·351
5·0	8·74	—	8·815	—	—	—	—	—
6·0	Crystallized	6·135	Crystallized	5·828	9·217	6·00	9·579	6·567
				6·04	—	—	—	—
8·0	—	—	—	—	Crystallized	6·366	Crystallized	6·968
10·0	—	—	—	—	—	—	—	—

to a mole number of $NaH_2PO_4,2H_2O$ mixed with 2 moles of H_3BO_3. The addition of a small amount of H_3BO_3 to $NaH_2PO_4,2H_2O$ showed the tendency that the thermal conversion of $NaPO_3$(II) into $Na_3(PO_3)_3$ was appreciably prevented.

H_3BO_3–KH_2PO_4–H_2O. This system has been studied from the freezing point to 40°C.[286] The only equilibrium solid phases are the starting components, which form a eutectic at $-3{\cdot}3$°C with a liquid phase composition of 2·6% H_3BO_3, 11·7% KH_2PO_4 and 85·7 %H_2O. It is claimed that complex borophosphates are formed in solution.[293]

H_3BO_3–$Ca(H_2PO_4)_2$–H_2O. The solubility of H_3BO_3 in $Ca(H_2PO_4)_2$ solution at 15°C was found to be reduced by raising the CaO and P_2O_5 concentrations in solution.[434] Minimum solubility was 1·67% B_2O_3.

H_3BO_3–$Mg(H_2PO_4)_2$–H_2O. Magnesium phosphates decrease the solubility of boric acid, but the acid has no marked affect on the solubility of the phosphates, although it prevents the hydrolysis of $Mg(H_2PO_4)_2$ and the precipitation of $MgHPO_4$.[435] Other workers confirmed that increasing the concentration of MgO and P_2O_5 brought about a decrease in H_3BO_3 solubility, both at 15° and at 80°C.[436]

H_3BO_3–NH_4VO_3–H_2O. Mutual solubility was studied at 25°, 30°, 35° and 45°C[437] and at 50°, 60°, and 75°C.[438] At below 26·2° the compound $B_2O_3,4V_2O_5,13NH_3,$-$29{\cdot}6H_2O$ formed.[437]

H_3BO_3–NaF–H_2O. Some dissolved states in this system were investigated potentiometrically using glass and fluoride ion-selective electrodes.[439] Formation constants of $BF(OH)_3^-$ and of $BF_2(OH)_2^-$ were determined.

H_3BO_3–KF–H_2O. In systems with $<1{\cdot}15\%$ H_3BO_3, $KF,2H_2O$ is the solid phase.[440] In systems containing 24·7–46·6% KF, a crystalline compound $K[B(OH)_3F]$ is formed.

H_3BO_3–LiCl–H_2O. The isotherm (25°C) has been constructed at $<45\%$ LiCl and $<5\%$ H_3BO_3.[441] The solubility of H_3BO_3 first decreases and after reaching a minimum of 1·91% in a solution containing 20·14% LiCl it increases; at 44·10% LiCl the solubility exceeds that in pure water (6·29 *vs.* 5·46% H_3BO_3).[442]

H_3BO_3–NaCl–H_2O. Molal volumes have been determined within the system.[464]

H_3BO_3–KCl–H_2O. The dependence of density, viscosity, pH and refractive index on equilibrium solutions of this system has been determined refractometrically.[443] The quaternary system with NaCl has been studied, along with the quinary system in which $MgCl_2$ was also present.[447]

H_3BO_3–RbCl–H_2O. An increase of H_3BO_3 solubility in the presence of RbCl, and a slight decrease of this due to the presence of H_3BO_3, were observed.[444] Density,

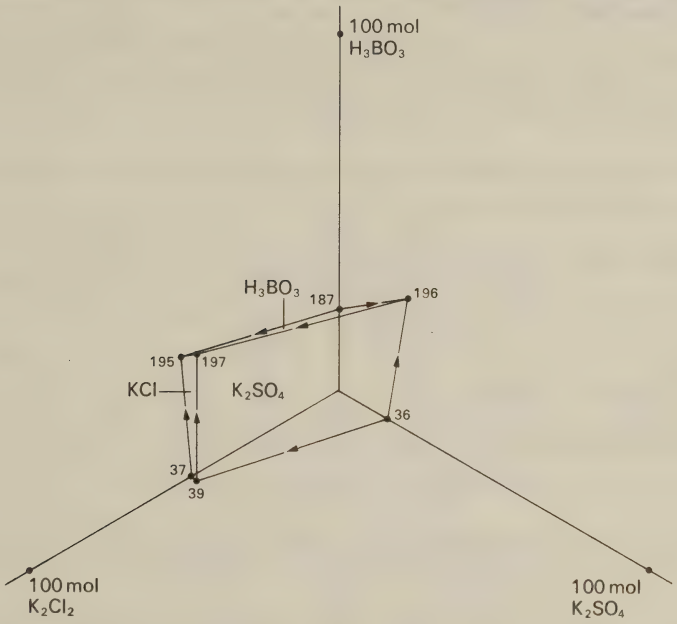


FIG. 39.—System KCl–K_2SO_4–H_3BO_3–H_2O at 35°C[265]

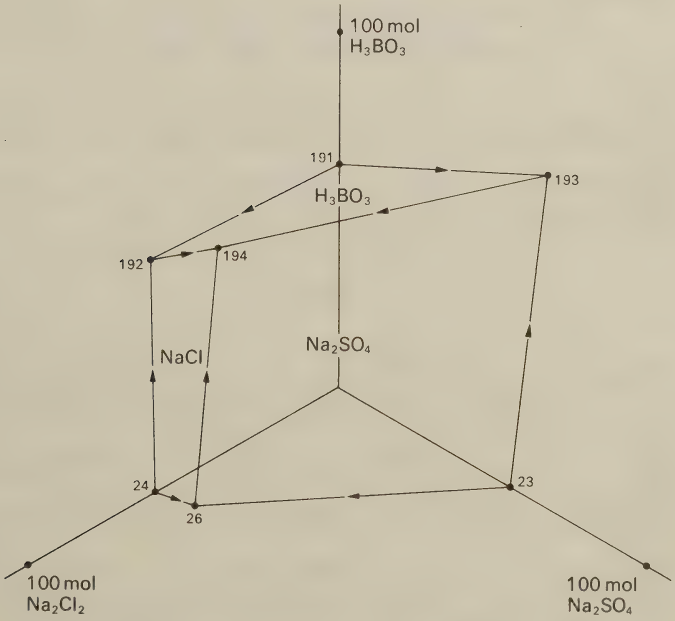


FIG. 40.—System NaCl–Na_2SO_4–H_3BO_3–H_2O at 75°C[265]

viscosity and refractive index data are given for equilibrium liquid phases containing up to 5·46% H_3BO_3 and 47·81% RbCl.

H_3BO_3–$MgCl_2$–H_2O. The system was studied at 25°C[281,428,433] and 70°C.[288] H_3BO_3 and $MgCl_2,6H_2O$ were the only solid equilibrium phases observed. Sorption processes in the system H_3BO_3–$MgCl_2$–$Zr(OH)_4$–H_2O have been investigated.[462] The quinary system H_3BO_3–$MgCl_2$–$MgSO_4$–HCl–H_2O was studied at 0°C[289]; and also H_3BO_3–$MgCl_2$–NaCl–KCl–H_2O.[447]

H_3BO_3–$CaCl_2$–H_2O. Part of this system is reported over a temperature range of 30°–80°C in connection with a patent for a process to produce boric acid from calcium borate ores.[290] The solubilities are summarized in Table LII. A cryoscopic study of

Table XLVIII.—Invariant Points in the System H_3BO_3–K_2SO_4–KCl–H_2O

Point	Solid phases	g/100 g H_2O				Mol/1000 mol H_2O			
		KCl	K_2SO_4	H_3BO_3	Total	K_2Cl_2	K_2SO_4	H_3BO_3	Total
37	KCl	39·0	—	—	39·0	47·1	—	—	47·1
36	K_2SO_4	—	14·1	—	14·1	—	14·5	—	14·5
187	H_3BO_3	—	—	7·9	7·9	—	—	22·8	22·8
39	KCl,K_2SO_4	38·4	1·7	—	40·1	46·4	1·7	—	48·1
195	KCl,H_3BO_3	41·0	—	11·6	52·6	49·4	—	33·6	83·0
196	K_2SO_4,H_3BO_3	—	21·2	12·5	33·7	—	21·9	36·4	58·3
197	KCl,K_2SO_4,H_3BO_3	39·9	2·8	12·1	54·8	48·2	2·9	35·1	86·2

Table XLIX.—Invariant Points in the System H_3BO_3–Na_2SO_4–NaCl–H_2O

35°C

Point	Solid phases	g/100 g H_2O				Mol/1000 mol H_2O			
		NaCl	Na_2SO_4	H_3BO_3	Total	Na_2Cl_2	Na_2SO_4	H_3BO_3	Total
6	NaCl	36·3	—	—	36·3	55·8	—	—	55·8
5	Na_2SO_4	—	50·7	—	50·7	—	64·2	—	64·2
187	H_3BO_3	—	—	7·9	7·9	—	—	22·8	22·8
8	NaCl,Na_2SO_4	33·6	9·3	—	42·9	51·8	11·7	—	63·5
188	NaCl,H_3BO_3	36·8	—	8·2	45·0	56·6	—	23·9	80·5
189	Na_2SO_4, H_3BO_3	—	53·0	13·1	66·1	—	67·1	38·1	105·2
190	NaCl, Na_2SO_4 H_3BO_3	33·2	11·9	9·6	54·7	51·1	15·1	28·0	94·2

75°C

Point	Solid phases	g/100 g H_2O				Mol/1000 mol H_2O			
		NaCl	Na_2SO_4	H_3BO_3	Total	Na_2Cl_2	Na_2SO_4	H_3BO_3	Total
24	NaCl	37·8	—	—	37·8	58·2	—	—	58·2
23	Na_2SO_4	—	43·9	—	43·9	—	55·6	—	55·6
191	H_3BO_3	—	—	21·1	21·1	—	—	61·2	61·2
26	NaCl,Na_2SO_4	35·5	6·8	—	42·3	54·7	8·6	—	63·3
192	NaCl,H_3BO_3	38·5	—	22·2	60·7	59·2	—	64·5	123·7
193	Na_2SO_4, H_3BO_3	—	51·7	31·4	83·1	—	65·5	91·0	156·5
194	NaCl,Na_2SO_4, H_3BO_3	35·5	12·4	25·0	72·9	54·6	15·7	72·6	142·9

boric acid in calcium chloride heptahydrate indicates that no dissociation or polymerization occurs,[291] which is surprising in view of the observation (above) that boric acid can be titrated as a strong acid in concentrated calcium chloride solution.

H_3BO_3–$BaCl_2$–H_2O. The system was studied at 25°C.[445]

H_3BO_3–NaBr–H_2O. A mutual lowering of the solubilities of components was observed in this system.[446] The univariant point of the system corresponds to maxima in density and refractive index and a minimum in pH.

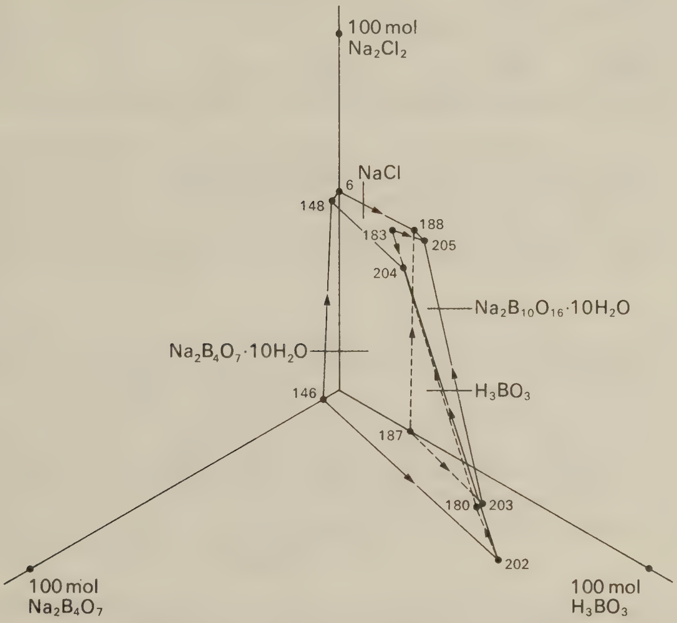


FIG. 41.—System NaCl–$Na_2B_4O_7$–H_3BO_3–H_2O at 35°C[265]

Table L.—Invariant Points in the System H_3BO_3–NaCl–$Na_2B_4O_7$–H_2O

Point	Solid phases	g/100 g H_2O				Mol/1000 mol H_2O			
		NaCl	$Na_2B_4O_7$	H_3BO_3	Total	Na_2Cl_2	$Na_2B_4O_7$	H_3BO_3	Total
6	NaCl	36·3	—	—	36·3	55·8	—	—	55·8
146	$Na_2B_4O_7.10H_2O$	—	5·3	—	5·3	—	4·7	—	4·7
187	H_3BO_3	—	—	7·9	7·9	—	—	22·8	22·8
148	NaCl,$Na_2B_4O_7$.-10H_2O	35·5	2·2	—	37·7	54·6	2·0	—	56·6
188	NaCl,H_3BO_3	36·8	—	8·2	45·0	56·6	—	23·9	80·5
202	$Na_2B_4O_7.10H_2O$, $Na_2B_{10}O_{16}.10H_2O$	—	23·6	24·7	48·3	—	21·0	71·6	92·6
203	H_3BO_3, $Na_2B_{10}O_{16}.10H_2O$	—	8·4	18·4	26·8	—	7·5	53·5	61·0
180	$Na_2B_{10}O_{16}.10H_2O$	—	9·9	18·3	28·2	—	8·9	53·1	62·0
183	NaCl, $Na_2B_{10}O_{16}.10H_2O$	36·1	3·7	6·9	46·7	55·6	3·3	20·0	78·9
204	NaCl,$Na_2B_4O_7$. 10H_2O, $Na_2B_{10}O_{16}.10H_2O$	34·6	10·1	10·0	54·7	53·3	9·0	29·0	91·3
205	NaCl,H_3BO_3, $Na_2B_{10}O_{16}.10H_2O$	36·3	1·2	9·4	46·9	55·8	1·0	27·4	84·2

Table LI.—Invariant Points in the System H_3BO_3–KCl–$K_2B_{10}O_{16}$–H_2O[265]

Point	Solid phases	g/100 g H_2O				Mol/1000 mol H_2O			
		KCl	$K_2B_{10}O_{16}$	H_3BO_3	Total	K_2Cl_2	$K_2B_{10}O_{16}$	H_3BO_3	Total
37	KCl	39·0	—	—	39·0	47·1	—	—	47·1
181	$K_2B_{10}O_{16}.8H_2O$	—	5·0	—	5·0	—	2·0	—	2·0
187	H_3BO_3	—	—	7·9	7·9	—	—	22·8	22·8
182	$KCl,K_2B_{10}O_{16}.8H_2O$	38·1	3·0	—	41·1	46·0	1·2	—	47·2
195	KCl, H_3BO_3	41·0	—	11·6	52·6	49·4	—	33·6	83·0
200	$K_2B_{10}O_{16}.8H_2O, H_3BO_3$	—	2·4	7·1	9·5	—	1·0	20·7	21·7
201	$KCl,K_2B_{10}O_{16}.8H_2O,H_3BO_3$	40·7	0·3	11·0	52·0	49·2	0·1	32·0	81·3

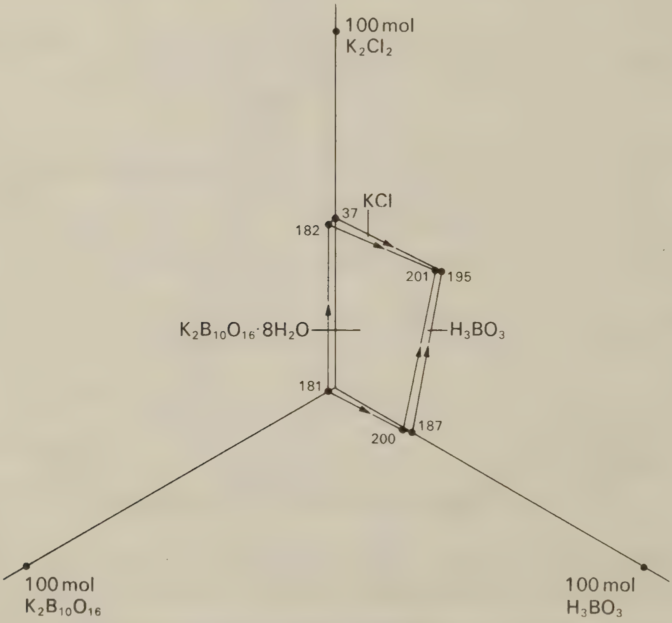


FIG. 42.—System KCl–$K_2B_{10}O_{16}$–H_3BO_3–H_2O at 35°C[265]

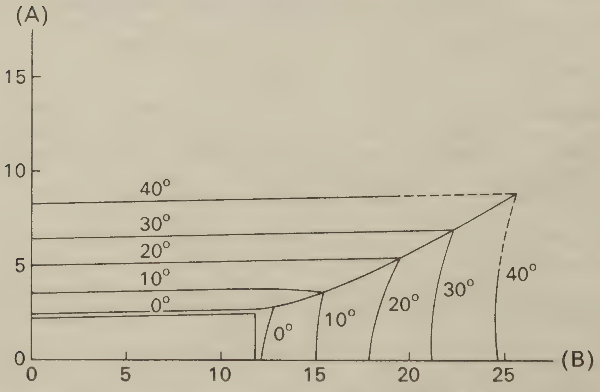


FIG. 42a.—Solubility diagram of the ternary system H_3BO_3–KH_2PO_4–H_2O. (A) % H_3BO_3 (by weight); (B) % KH_2PO_4 (by weight)[286]

Table LII.—Solubility of Orthoboric Acid in $CaCl_2$ Solutions[290]

g $CaCl_2$/100 g H_2O	g H_3BO_3/100 g H_2O at various temperatures					
	30°C	40°C	50°C	60°C	70°C	80°C
0·0	6·7	8·7	11·5	14·8	18·6	23·6
4·8	5·9	7·9	10·3	13·4	17·3	22·1
15·0	4·4	5·9	7·8	10·2	13·3	—
28·7	—	4·7	6·3	8·5	11·3	15·1
42·0	3·0	4·2	5·6	7·5	9·7	13·7
56·2	2·8	3·8	5·2	7·0	9·1	12·0
71·0	3·4	4·3	5·5	7·3	9·6	11·5
108·3	—	5·7	7·0	9·0	11·5	14·1
130·0	—	—	9·2	10·9	13·7	17·1

H_3BO_3–acetic acid–H_2O. Acetic acid has a salting-out effect on the solubility of boric acid. Stabilization of metaboric acid was observed in such a system, indicating a slow hydration process.[432] So-called diboric oxide tetraacetate, $B_2O(OAc)_4$, has been prepared and its reactions with metal acetates studied.[473] A batch or continuous process for the production of boron acetate from boric acid and acetic anhydride has been described.[478]

H_3BO_3–oxalic acid–H_2O. In a similar phase study applied to this system it was found that metaboric acid did not hydrate in concentrated aqueous solutions of oxalic acid, but did so in more diluted ($\leq 50\%$) solutions.[432] The solubility of orthoboric acid has been determined from 55°C down to the freezing point.[474] A cryohydrate point occurs at $-2{\cdot}1°$ and has the composition H_3BO_3 3·3%, $H_2C_2O_4$ 4·3%, and H_2O 92·4%. As the temperature is increased, relatively more oxalic than boric acid goes into solution, but at constant temperature there is an increase in mutual solubility which may be attributable to the formation of boro-oxalate complexes. The existence of such complexes had been discussed in earlier work.[475–6]

H_3BO_3–tartaric acid–H_2O. This system was reported to display no complex compounds as equilibrium solid phases, although viscosity, density, and electrical conductivity of the solutions suggest the formation of 1:1 and 1:2 complexes in solution.[296, 362–4] One of the schools later reported the existence of $H_3BO_3,2H_2C_4H_4O_6$.[477] The solubility of boric acid is increased by the presence of tartaric acid. Thermogravimetric study of mixtures of boric acid and tartaric acid suggest the formation of a 1:1 complex.[308] Melting point diagrams have been constructed and the existence of a complex conjectured in such higher temperature systems.[481]

H_3BO_3–citric acid–H_2O. Studies including complex formation, solubility, density, viscosity and refractive index established that the solubility diagram has three crystallization branches corresponding to the parent acids and $H_3BO_32H_3C_6H_5O_7$.[420]

H_3BO_3–urea–H_2O. No evidence of compound formation was found in the earlier studies of this system.[300, 301] The ternary eutectic was reported to be at -14°C, with a liquid composition of 3·7% H_3BO_3, 36·5% urea, and 59·8% H_2O. The solubility of urea in the system is little influenced by the H_3BO_3,[300] but the solubility of boric acid is doubled with urea[301] at 30°C. The density and viscosity of the solutions vary additively.[301] More recently, a binary compound $H_3BO_3,2CO(NH_2)_2$ was reported to be formed at 52°–75°C.[401, 402]

H_3BO_3–thiourea–H_2O. This system has been examined at 25°C.[302] The solubilities of each of the two solids is relatively unaffected by the presence of the other; however, there is some evidence for the formation of solid solutions of thiourea in boric acid.

NON-AQUEOUS SOLUTIONS OF BORIC ACID

Boric acid is soluble in many non-aqueous solvents, especially hydroxylated organic compounds. Often this solubility is a result of reaction, and these cases are discussed in more detail elsewhere in this volume under the heading appropriate to the reaction product; Section A17 is devoted to esters of boric acid. Earlier studies are summarized in Mellor,[82] where it is illustrated that the solubility in mixtures of the lower aliphatic alcohols and water shows a minimum at certain ratios of water to alcohol. Nikolaev and Kurnakova[303] have reported values for several organic solvents at 20° and 25°C, as shown in Table LIII. Additional data are given by Schneider.[304] Data for surface tension and viscosity of solutions of boric acid in methanol are given by Kozakevich.[365]

Semenchenko[359] has predicted that the solubility of a substance has a maximum at some medium dielectric constant of the solvent; the greater the polarity of the solute, the higher the dielectric constant at maximum solubility. Boric acid is shown to fit this predicted behaviour, with the data shown in Table LIIa.

Sciarra[335, 373] has examined the solubility of boric acid in a number of organic solvents useful in pharmacy. His results at 25°C are shown in Table LIIIa.[335] He has made a detailed study of the system H_3BO_3–sorbitol–H_2O; the results of solubility and specific gravity in the system are summarized in Tables LIIIb and LIIIc.[373]

Early work on the effect of organic solvents on the dissociation of boric acid in aqueous solutions has been reviewed in Mellor.[82] Further studies have been made.[360, 361] Aleksandrov *et al.* report pK's for boric acid as 13·23 in 50:50 methanol–benzene and 11·36 in 47:47:6 methanol–benzene–water.[361]

The solubility of boric acid in liquid ammonia is reported to be 1·92 g/100 g NH_3 at 25°C.[305] It is said to be insoluble in liquid sulphur dioxide.[306]

H_3BO_3–formamide; H_3BO_3–dimethylformamide. Orthoboric acid reacts with both formamide and dimethylformamide (DMF) to form formic acid, water and the corresponding amine pentaborate.[297, 298] This reaction accounts for the thick anodic films formed on aluminium.[307] When metaboric acid (II or III) is dissolved in cold dimethylformamide and the solvent evaporated under vacuum, $2HBO_2$,DMF is obtained[298];

Table LIIa.—Solubility of Boric Acid in Several Solvents at 20°C[354]

Solvent	mol fraction H_3BO_3
Water	0·014
96·5% formic acid	0·017
Glycerol	0·271
Glycol	0·206
Methanol	0·125
Acetone	0·103
150-amyl alcohol	0·059

Table LIII.—Solubility of Boric Acid in Some Organic Solvents

Solvent	Temp. °C	% H_3BO_3
Methanol	20	20·68
Acetone	20	0·57
Methyl ethyl ketone	20	0·7
Methyl butyl ketone	20	0·23
Isoamyl alcohol	25	2·39
Ethyl acetate	20	1·0
Fusel oil	25	2·46
Aniline	20	0·15

Table LIIIa.—Solubility of Boric Acid in Various Solvents at 25°C[335]

Solvent	Solubility			Specific gravity	
	ml solvent/g solute	% wt.	% volume	Solvent	Saturated solution boric acid
Water	18·08	5·24	5·35	1·0000	1·0203
Propylene glycol	5·44	15·06	16·23	1·0360	1·0774
Polyethylene glycol 400	11·37	7·82	8·97	1·1230	1·1470
Polyethylene glycol 600	16·51	5·38	6·13	1·1250	1·1399
Sorbo	3·45	22·27	28·80	1·3023	1·2933
Dextrose-10%	18·31	5·27	5·55	1·0363	1·0524
Dextrose-25%	19·23	4·78	5·25	1·0884	1·0977
Mannitol-10%	14·64	6·62	6·96	1·0325	1·0517
Maltose-10%	18·15	5·32	5·61	1·0351	1·0541
Lactose-10%	17·86	5·42	5·71	1·0346	1·0533
d-Levulose 10%	18·10	5·33	5·63	1·0369	1·0559
d-Levulose Syrupy	19·17	4·08	5·09	1·2786	1·2470
Glycerin	3·89	17·55	22·29	1·2454	1·2703

Table LIIIb.—Composition of Boric Acid–Water–Sorbitol System at Various Temperatures[373]

Composition								
Boric acid, %	Sorbitol, %	Water, %	Boric acid, %	Sorbitol, %	Water, %	Boric acid, %	Sorbitol, %	Water, %
21°			25°			30°		
5·03	0·00	94·97	5·57	0·00	94·43	6·36	0·00	93·64
5·74	4·76	89·50	6·31	4·68	89·01	7·21	4·64	88·15
6·70	9·33	83·97	7·09	9·29	83·62	7·99	9·20	82·81
7·33	13·90	78·77	7·87	13·82	78·31	8·76	13·69	77·55
8·37	18·33	73·30	8·72	18·26	73·02	9·63	18·07	72·30
9·09	22·73	68·18	9·47	22·63	67·90	10·45	22·30	67·19
9·88	27·04	63·08	10·42	26·87	62·71	11·31	26·61	62·08
10·68	31·26	58·06	11·18	31·09	57·73	12·11	30·76	57·13
11·22	35·51	53·27	11·63	35·47	52·90	12·64	34·94	52·42
12·03	39·49	43·38	12·92	39·19	47·89	13·86	38·76	47·38
12·87	43·57	43·56	13·80	43·10	43·10	14·72	42·64	42·64
13·99	47·31	38·70	14·98	46·76	38·26	15·89	46·26	37·85
15·28	50·83	33·99	16·17	50·30	33·53	17·02	49·79	33·19
16·45	54·31	29·24	17·31	53·75	28·94	18·32	53·09	28·59
17·43	57·80	24·77	18·66	56·96	24·38	19·47	56·37	24·16

similarly by dissolving the metaboric acids in boiling DMF and cooling the solution. It has been claimed that boric acid solutions in DMF can be titrated with lithium isopropoxide solutions, although the significance of the titre is open to question.[299]

SOLVENT EXTRACTION OF BORIC ACID FROM AQUEOUS SOLUTIONS

The solubility of boric acid in various organic solvents that are immiscible with water has been studied as a means of separating boric acid from aqueous solutions. Vinogradov and Azarova[309] have determined the distribution constant of boric acid for a number of organic liquids at 25°C. Their results for water solutions are shown in Table LIV. The effect of magnesium chloride on the distribution constant is shown in Table

Table LIIIb.—continued

40°			50°			60°		
8·09	0·00	91·91	9·98	0·00	90·02	12·65	0·00	87·35
8·95	4·55	86·50	10·59	4·45	84·60	13·46	4·33	82·21
9·78	9·02	81·20	11·76	8·82	79·42	14·25	8·58	77·17
10·64	13·40	75·96	12·84	13·07	74·09	15·00	12·75	72·75
11·55	17·69	70·76	13·56	17·29	65·15	16·00	16·80	67·20
12·46	21·89	65·65	14·43	21·39	64·18	16·88	20·78	62·34
13·14	26·06	60·80	15·26	25·42	59·33	17·80	24·66	57·54
14·02	30·07	55·91	16·33	29·28	54·39	18·60	28·84	52·56
14·53	34·19	51·28	16·69	33·34	49·97	19·57	32·57	47·86
15·83	37·88	46·29	17·97	36·91	45·12	20·52	35·77	43·71
16·67	41·67	41·66	18·94	40·53	40·53	21·76	39·13	39·11
17·87	45·17	36·96	20·02	43·99	35·99	22·60	41·47	35·93
18·91	48·65	32·44	21·31	47·21	31·48	23·63	45·22	30·15
20·27	51·82	27·91	22·30	50·51	27·19	24·48	49·09	26·43
24·20	52·96	22·84	23·74	53·38	22·88	25·65	52·05	22·30

Table LIIIc.—Specific Gravity of Saturated Solution of Boric Acid in Sorbitol Solution at Various Temperatures[373]

Concentration of sorbitol, % w/w	Specific gravity					
	21°	25°	30°	40°	50°	60°
0	1·018	1·020	1·023	1·029	1·036	1·046
5	1·036	1·038	1·041	1·047	1·053	1·061
10	1·056	1·056	1·059	1·064	1·071	1·079
15	1·074	1·075	1·077	1·082	1·084	1·096
20	1·095	1·095	1·096	1·101	1·108	1·114
25	1·113	1·114	1·116	1·120	1·124	1·131
30	1·134	1·134	1·140	1·140	1·145	1·150
35	1·152	1·152	1·154	1·157	1·163	1·167
40	1·165	1·164	1·166	1·170	1·171	1·187
45	1·190	1·191	1·192	1·194	1·197	1·206
50	1·211	1·210	1·210	1·210	1·214	1·221
55	1·231	1·231	1·232	1·234	1·235	1·240
60	1·253	1·252	1·252	1·254	2·257	1·258
65	1·274	1·272	1·272	1·271	1·273	1·272
70	1·294	1·292	1·293	1·291	1·290	1·294

LV; it is evident that magnesium chloride has a 'salting out' effect on boric acid, increasing its relative solubility in the organic phase for most cases. The distribution of boric acid between isoamyl alcohol and water at temperatures from 15° to 45°C has been investigated.[337] The distribution is found to be substantially independent of temperature over the range studied, as illustrated in Fig. 43.

The effect of hydrochloric acid on the distribution of boric acid between water and isoamyl alcohol has been studied.[310] The region of immiscibility in the system disappears as the concentration of hydrochloric acid increases, as indicated in Fig. 43a. Table LVa summarizes the effect of hydrochloric and boric acid concentrations on their respective distribution constants in the system. The presence of hydrochloric acid increases the relative concentration of boric acid in the organic phase. The effect of temperature on the distribution constant for boric acid between isoamyl alcohol and aqueous solutions containing chlorides of magnesium, lithium, sodium, potassium, and cæsium has been studied at 25°, 50°, and 75°C.[311] The distribution constant increases with temperature for solutions containing chlorides of sodium, potassium and caesium, but decreases with increasing temperature for all the others. It is suggested that the

Table LIV.—Extraction of Boric Acid from Aqueous Solutions[309]

Extracting agent	H_3BO_3	Extracting agent	H_3BO_3
Hexane	0·00	DOMP[a]	0·10
Dodecane	0·00	n-Dodecanol	0·13
Hexadecane	0·00		
Cyclohexane	0·00	n-Decanol	0·14
Benzene	0·00	n-Nonanol	0·16
Toluene	0·00	n-Octanol	0·18
Chloroform	0·00	Ethyl acetate	0·21
Nitrobenzene	0·00	n-Hexanol	0·23
Chlorobenzene	0·00		
Tetrachloromethane	0·00	Benzyl alcohol	0·23
Cyclohexanone	0·00	Cyclohexanol	0·24
Acetophenone	0·00	TBP[b]	0·28
Trioetylamine	0·03	3-Methylbutanol	0·28
Butyl acetate	0·05	n-Pentanol	0·30
Pentyl acetate	0·06	2-Methylpropanol	0·36
Dibutyl ether	0·06	n-Butanol	0·42
		D-PMP[c]	0·52

[a] DOMP = dioctyl methyphosphonate
[b] TBP = tributyl phosphate.
[c] D-PMP = di-isopentyl methylphosphonate.

Table LV.—Extraction of Boric Acid from Magnesium Chloride Solutions[309]

Extracting agent	aq $^{c}MgCl_2$ M	$^{a}H_3BO_3$	$^{a}MgCl_2$	β	Extracting agent	aq $^{c}MgCl_2$ M	$^{a}H_3BO_3$	$^{a}MgCl_2$	β
n-Butanol	—	0·42	—	∞	3-Methyl-	3·06	1·16	0·013	89
	1·11	0·60	0·018	33	butanol	3·99	2·41	0·036	67
	2·18	0·84	0·025	34	(*contd*)	4·41	4·40	0·060	73
	3·99	1·79	0·117	15		4·65	5·66	0·079	72
	4·94	4·00	0·232	17					
					n-Nonanol	—	0·16	—	∞
2-Methyl-	—	0·36	—	∞		1·00	0·26	0·0005	520
propanol	1·12	0·50	0·0063	79		1·86	0·45	0·0011	408
	1·60	0·62	0·0069	90		2·18	0·50	0·0014	357
	2·69	1·00	0·0085	117		2·56	0·77	0·0034	226
	2·89	1·12	0·011	102		3·77	1·67	0·016	104
	4·71	5·30	0·116	46		4·05	1·95	0·025	78
						5·10	1·78	0·037	48
	—	0·30	—	∞					
n-Pentanol	1 11	0·41	0·0036	114	TBP[a]	—	0·28	—	∞
	2·21	0·82	0·0060	137		1·44	0·43	0·00017	2530
	2·94	1·07	0·010	107		2·14	0·55	0·00024	2290
	5·07	4·29	0·113	38		3·75	0·87	0·0057	153
						4·61	0·82	0·027	30
3-Methyl-	—	0·28	—	∞					
butanol	0·93	0·40	0·0011	364	DPMP[b]	—	0·52	—	∞
	1·64	0·54	0·0026	208		0·94	0·82	0·019	43
	1·88	0·64	0·0034	188		1·73	1·00	0·053	19
	2·17	0·71	0·0046	154		4·68	0·59	0·214	2·7

[a] TBP = Tributyl phosphate.
[b] DPMP = di-isopentylmethyl phosphate.

differences in behaviour are associated with differences in hydration of the respective cations. Other studies of this system have been made,[312–14] including its use in separating boron isotopes.[314]

The distribution of boric acid between aqueous solutions and octanol has been studied.[315] Ethyl ether has been studied as an extractive solvent for boric acid[316–18] in connection with studies on the recovery of uranium values from ores and process

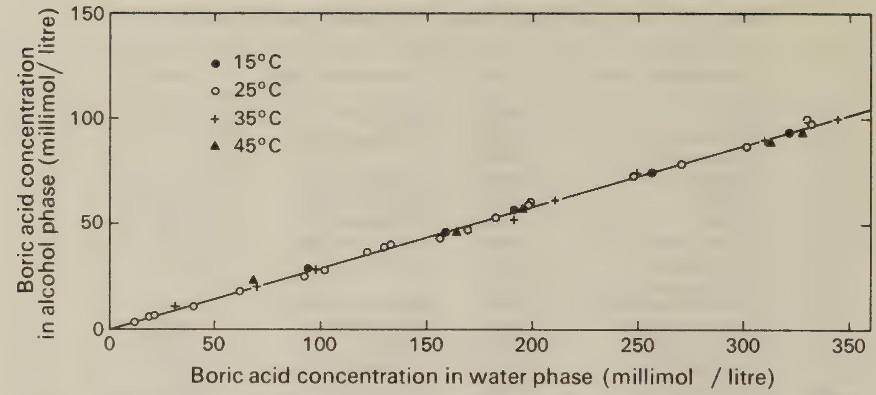


FIG. 43.—Equilibrium distribution of boric acid between isoamyl alcohol and water[337]

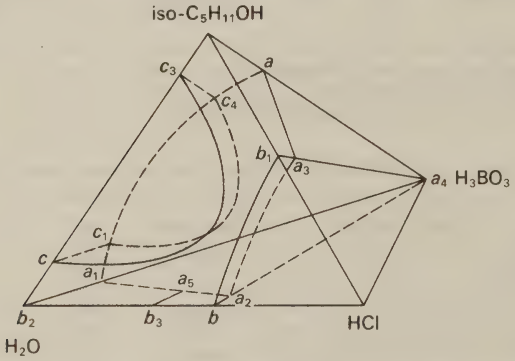


FIG. 43a.—Representation of the H_3BO_3–HCl–H_2O–iso-$C_5H_{11}OH$ system[310]

solutions. The distribution constant ($C_{ether}/C_{aqueous}$) is reported to be 0·056.[317] The results of Bachelet *et al.*[316] are summarized in Table LVI.

A study of the distribution of boric acid between tri-*n*-butyl phosphate and aqueous solutions suggests that the mechanism of solution in the ester is the formation of a 1:2 complex between boric acid and the ester.[319] The effect of magnesium chloride is to increase the concentration of boric acid in the organic phase, as illustrated in Fig. 44. The effect of temperature on the distribution constant follows the relationship:

$$d \ln k/dT = \Delta H/RT^2$$

Values of ΔH were −0·49 and −0·53 kcal/mol for boric acid concentrations of 0·51 and 1·35 g/litre, respectively. The effect of other acids varies with their concentration, at first decreasing, then increasing, and finally decreasing the distribution constant, as shown in Fig. 45. The explanation for the initial decrease is unknown, but the increase is postulated as a 'salting in' of the organic phase; the subsequent decrease is postulated to be a 'salting out' of the organic phase as the concentration of the acid becomes high there.

The industrial implications and implementation of solvent extraction as a means of recovering or removing borates from aqueous solutions and brines are discussed in the following section (A7). The favoured reagents are aliphatic diols[469, 470] and naphthalene diols.[471, 472]

BORON-SPECIFIC ION-EXCHANGE RESINS AND ADSORBENTS

The use of ion-exchange resins for the removal of boron from aqueous solutions, especially from dilute solution, has been well investigated. Kunin, Preuss *et al.* de-

Table LVa.—Distribution of Orthoboric Acid Between Hydrochloride Acid Solutions and Isoamyl Alcohol[310]

Concentration in aqueous phase, wt. %		Distribution constants		Concentration in aqueous phase, wt. %		Distribution constants		Concentration in aqueous phase, wt. %		Distribution constants	
H_3BO_3	HCl	H_3BO_3	HCl	H_3BO_3	HCl	H_3BO_3	HCl	H_3BO_3	HCl	H_3BO_3	HCl
0·09		0·27	—	0·23	3·21	0·34	0·078	0·51	12·21	0·43	0·30
0·38		0·28	—	0·52	3·23	0·34	0·078	1·04	12·22	0·43	0·30
0·90	—	0·28	—	1·55	3·21	0·34	0·078	1·98	12·18	0·42	0·30
1·81	—	0·28	—	2·63	3·22	0·34	0·078	2·77	12·07	0·40	0·30
2·88	—	0·28	—	4·41	3·22	0·34	0·078	0·55	16·43	0·45	0·40
3·66	—	0·29	—	0·45	6·65	0·39	0·16	1·42	16·44	0·45	0·40
5·19	—	0·28	—	0·97	6·65	0·39	0·16	2·27	16·79	0·44	0·40
0·92	1·78	0·32	0·046	2·04	6·65	0·39	0·16	0·44	22·11	0·50	0·58
3·14	1·78	0·32	0·046	3·67	6·63	0·38	0·16	0·95	22·12	0·50	0·58
								1·89	22·06	0·49	0·58

Table LVI.—Distribution of Orthoboric Acid Between Water Solutions and Diethyl Ether[316]

Solvent	Temp.	Soly. of H_3BO_3 (g/100 g solvent)
Et_2O (anhyd.)	12°	0·074
Et_2O (satd. with H_2O)	14°	0·1
$Et_2O + 7{\cdot}2$ g $UO_2(NO_3)_2.6H_2O$	16°	0·16
$Et_2O + 6{\cdot}6$ g $UO_2(NO_3)_2.6H_2O$	18°	0·14

H_3BO_3 g	H_2O ml	Et_2O ml	Temp.	Partition coefficient
0·34	10	100	15°	0·038
0·36	10	100	12°	0·035
0·2	10	100	14°	0·024
0·072	10	100	14°	0·025
0·072	10	100	14°	0·028

veloped and patented[320,321] a boron-specific ion-exchange resin based on a chloromethylated styrenedivinyl benzene copolymer, which has been aminated with *N*-methyl glucamine. It is known commercially by the Rohm and Hass trade name 'Amberlite XE-243'. This resin has a high capacity for boron absorption as shown in Table LVIIa, b which compares it with several other commercial ion-exchange resins, and illustrates the effect of other solutes on the absorption in terms of boron concentration in the solution before and after a single pass through the resin bed. Resin capacity as affected by regeneration and other constituents of the solution in terms of grams of boron per litre of resin (at 10% boron leakage) is shown in Table LVIIIa, b. Studies involving the use of Amberlite XE-243 have been published[465,466] and the preparation and performance of closely similar resins have been described.[467]

Other workers have studied different types of ion-exchange resin for the removal or concentration of boric acid from aqueous solutions; including the resins 'Amberlite IRA-400',[322] 'IRA-410',[322,323] 'EDE-10P',[324] and 'Amberlite JR-120'.[328] It has been pointed out that the boron capacity of an anion-exchange resin of a strong-base type varies considerably with the boron concentration in the solution.[326,329,425] This is attributed to the presence of polymeric anions in solutions at higher concentrations.

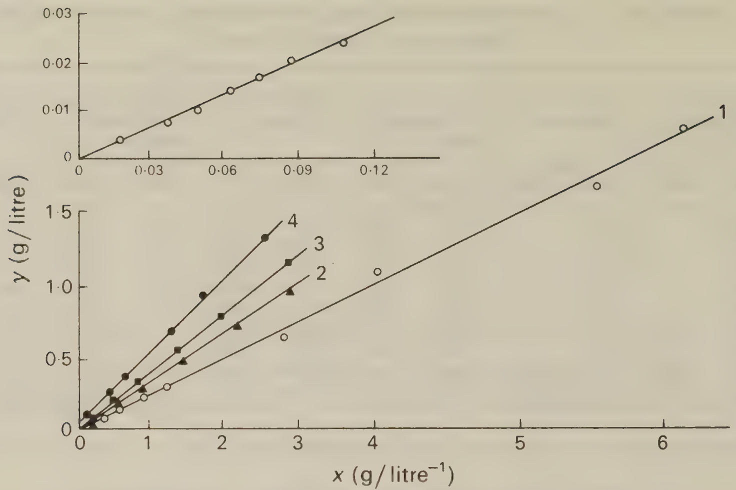


FIG. 44.—Partition isotherms for boric acid.[319] (1) Without salting-out agent; (2)–(4) In the presence of magnesium chloride; $MgCl_2$ concentrations: (2) 0·28 M; (3) 0·94 M; (4) 1·58 M

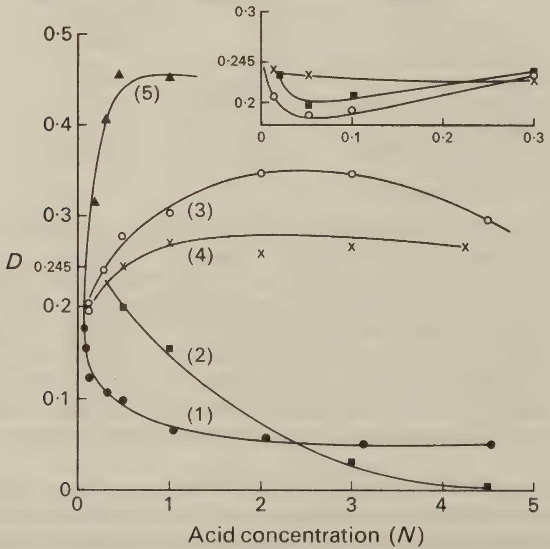


FIG. 45.—Extraction of boric acid in the presence of inorganic acids.[319] H_3BO_3 concentration 0·11 g/litre: (1) $HClO_4$; (2) HNO_3; (3) HCl; (4) H_2SO_4; (5) HF

A sorbitol-based borate-specific resin has also been made.[468] Ion-exchange resins have been studied in the separation of boron isotopes; often glycerol is added to the solution in this work.[325–7, 330] α values of the order of 1·016–1·018 have been obtained. Ion-exchange resins have been used to prepare high-purity boric acid solutions by passing the solution through a resin bed to remove impurity ions, especially iron, but to allow the boric acid to pass through.[328, 331, 332]

The use of charcoal as an adsorbent for boric acid from aqueous or alcoholic solution has been studied[333]; capacities ranged from 11·5 to 30·8 milligrams of boric acid per gram of bone charcoal at 10°C for boric acid concentrations ranging from 2·91 to 11·60 g/litre. However, the most extensively studied adsorbent for boric acid is magnesium oxide, the use of which in removing borate ions from aqueous solutions such

Table LVIIa.—Comparison of Boron-Specific Resin with Conventional Anion Exchange Resin for Adsorbing Boron[321]

Resin	Ionic form	Solution conc., p.p.m. B	
		Before	After
Boron-specific resin	Free base	10·8	0·0
	Chloride	10·8	0·0
Amberlite IR-45	Free base	10·8	10·7
	Chloride	10·8	10·8
Amberlite IRA-401	Hydroxide	10·8	5·0
	Chloride	10·8	10·8

[a] Batch adsorption from 500-p.p.m. solution of NaCl.

Table LVIIb.—Batch Adsorption of Boron by Boron-Specific Resin from Various Solutions[321]

Solution	Solution conc., p.p.m. B	
	Before	After
10% H_2SO_4	10·8	3·2
4% HCl	10·7	2·9
0·2 M NaH_2PO_4	10·8	1·9
0·2 M Na_2HPO_4	10·4	0·5
4% NaOH	10·4	0·6
4% NH_4OH	11·3	1·5
500 p.p.m. $CaCl_2$	10·9	0·0
Deionized water	10·7	0·0

Table LVIIIa.—Regeneration of Boron-Specific Ion Exchange Resin[321]

H_2SO_4, Conc., %	Column capacity,[a] g B/litre resin		
	3 lb[b] H_2SO_4	6 lb[b] H_2SO_4	12 lb[b] H_2SO_4
2	0·3	0·4	3·9
5	0·9	4·2	—
10	3·6	3·5	3·7

[a] Breakthrough capacity corresponding to 10% boron leakage using 500 p.p.m. NaCl containing 10 p.p.m. B.

[b] lb. H_2SO_4 per cubic foot of resin followed by 2 lb NH_3 (as 4% NH_4OH).

Table LVIIIb.—Column Capacity[a] of Boron-Specific Ion Exchange Resin[321]

Influent	Capacity g B/litre resin
10 p.p.m. B as H_2BO_2	3·6
500 p.p.m. NaCl + 10 p.p.m. B	3·6
500 p.p.m. $NaHCO_3$ + 10 p.p.m. B	3·6
12% $MgCl_2$ + 100 p.p.m. B	2·8

[a] Capacity at 10% leakage following regeneration with 3 lb H_2SO_4 (10%) and 2 lb NH_3 (4%) per cubic foot of resin.

Table LIX.—Fluorescence and Phosphorescence of Some Organic Molecules in Boric Acid[380]

No.	Activator	Fluorescence of activator (u.v. excitation)	Luminiscence (ultra-violet)						Intensity of phosphorescence (activator 1·0 mg)
			1·0 mg		0·1 mg		0·01 mg		
			Fluorescence	Phosphorescence	Fluorescence	Phosphorescence	Fluorescence	Phosphorescence	
	O-Hydroxy-carbonyl compounds								
1	Resacetophenone	Green	Blue	Blue	Blue	Blue	Blue	Blue	Strong
2	γ-Resacetophenone	Dull yellow	Green	Green	Bluish-green	Bluish-green	Bluish-green	Bluish-green	Moderately strong
3	ω-Methoxy- ,,	Greenish-yellow	Yellow	Yellow	Light blue	Light blue	Light blue	Light blue	Weak
4	Phloracetophenone	Dull yellow	Yellowish-green	Yellowish-green	Yellowish-green	Yellowish-green	—	—	Very weak
5	β-Resorcylic aldehyde	Nil	Yellow	Yellow	Light blue	Light blue	Nil	?	Very weak
6	3-methyl- ,, ,,	Yellow	Yellow	Yellow	Light yellow	Yellow	Pale yellow	Yellow	Very weak
7	Benzoyl-phloroglucinaldehyde	Dull yellow	Orange-yellow	Light yellow	Light orange-yellow	Light yellow	Nil	Light yellow	Very weak
8	Methyl-2:4-dihydroxy-3-formyl benzoate	Dull yellow	Light greenish-yellow	Light greenish-yellow	Very light greenish-yellow	Very light greenish-yellow	Nil	?	Very weak
9	7-Hydroxycoumarin-8-aldehyde	Deep yellow	Pale green	Green	Green	Green	Nil	?	Weak
10	7-Hydroxy-3-methoxy-flavone-8-aldehyde	Deep yellow	Blue	Blue	Blue	Blue	Nil	?	Mod. strong
11	Salicylic acid	Deep blue	Violet	Blue	Violet	Blue	Nil	Blue	Mod. strong
12	Sulphosalicylic acid	Deep blue	Violet	Greenish-blue	Violet	Greenish-blue	—	—	Mod. strong
13	β-Resorcylic acid	Light blue	Blue	Blue	Blue	Blue	Nil	Pale blue	Weak
14	1-Hydroxy-2-naphthoic acid	Deep blue	Deep violet-blue	Deep greenish-yellow	Violet-blue	Greenish-yellow	Light violet-blue	Greenish-yellow	Very strong
15	2-Hydroxy-3-naphthoic acid	Lemon-yellow	Green	Yellow	Green	Yellow	Green	Yellow	Very weak
16	Ethyl orsellinate	Violet-blue	Light blue	Light blue	Light blue	Light blue	Nil	Light blue	Very weak
	Phenols								
17	Catechol	Nil	Nil	Pale blue	—	—	—	—	Very weak
18	Resorcinol	Nil	?	Pale blue	—	—	—	—	Very weak

19	Hydroquinone	Violet-blue	?	Pale blue	—	—	—	—	Very weak
20	Pyrogallol	Nil	Nil	Pale blue	—	—	—	—	Very weak
21	Phloroglucinol	Blue	Pale blue	Pale blue	—	—	—	—	Very weak
22	α-Naphthol	Nil	Violet	Pale blue	—	—	—	—	Weak
23	β-Naphthol	Nil	Nil	Cream coloured	—	—	—	—	Very weak
	Umbelliferone and derivatives								
24	Umbelliferone	Light violet-blue	Deep violet	Greenish-yellow	Violet	Greenish-yellow	Light violet	Greenish-yellow	Very strong
25	4-Methyl-umbelliferone	Deep violet	Deep violet	Bluish-green	Violet	Bluish-green	Light violet	Bluish-green	Very strong
26	4:8-Dimethyl-umbelliferone	Nil	Deep violet	Deep green	Violet	Deep green	Bluish-violet	Deep green	Very strong
27	8-Allyl-umbelliferone	Blue	Deep violet-blue	Greenish-yellow	Violet blue	Greenish-yellow	Light violet-blue	Pale green	Very strong
28	5-Methyl-3-carboxyethyl-umbelliferone	Green	Deep violet-blue	Greenish-yellow	Violet blue	Greenish-yellow	Light violet-blue	Pale green	Very strong
	Miscellaneous compounds								
29	Vanillin	Nil	Greenish-yellow	Pale blue	—	—	—	—	Very weak
30	Isovanillin	Nil	Blue	Blue	—	—	—	—	Very weak
31	*m*-hydroxy-benzoic acid	Bluish-pink	Greenish-yellow	Greenish-yellow	—	—	—	—	Strong; greater than with salicylic acid
32	*p*-Hydroxy-benzoic acid	Blue	Pale violet	Blue	—	—	—	—	Moderately strong; less than with salicylic acid
33	Mandelic acid	Nil	Nil	Pale blue	—	—	—	—	Very weak
34	Benzoin	Orange-yellow	Nil	Pale blue	—	—	—	—	Very weak
35	2-Methyl-3-methoxy-7-hydroxy-chromone	Nil	Deep violet	Yellow	Deep violet	Yellow	Deep violet	Yellow	Strong
36	3-Benzoyl-7-hydroxy-flavone	Nil	Greenish-yellow	Pale blue	Pale green	Pale blue	Pale green	Pale blue	Strong
37	6:8-Diallyl-7-hydroxy-flavone	Yellow	Greenish-yellow	Greenish-blue	Greenish-blue	Greenish-blue	Greenish-blue	Greenish-blue	Moderately strong

as brines and mineral waters is described in numerous articles and patents.[449–54] The mechanism of adsorption has been investigated in considerable detail, some workers believing either that $Mg(OH)_2$ acts as an ion-exchanger or that there is a structure change in the crystal lattice.[455] Others consider compound formation to be more likely with the hydroxides of magnesium and other divalent metals, where the anions tend to be polyborates rather than simple orthoborates.[456] Rates of sorption of boric oxide on magnesium have been measured[457] and a laboratory method of determining the activity of magnesium oxide has been developed.[426] Adsorption is greatly influenced by the origin, and especially the temperature of calcination, of the magnesia.[455, 457–61] Magnesite, brucite marble and dolomite are all effective when calcined.[455, 458–61] The presence of sulphate anion interferes with borate adsorption.[458] The sorption diagram of the complex system H_3BO_3–$MgCl_2$–$Zr(OH)_4$–H_2O has been described.[462]

Boric acid is adsorbed on clays and other soil constituents; the adsorption follows the Langmuir adsorption isotherm,[366] and is affected by other constituents in the soil solution, such as calcium ion, or pH.

The chromatographic behaviour of boric acid and borates on Whatman No. 1 filter paper has been studied,[334] using a wide variety of solvents and other components. No evidence for separation of polymeric borate ions could be found, and R_f appeared to be affected primarily by the acidity of the medium, in the absence of materials forming complex ions with borates. The formation of complex borate ions, such as borotungstates, was demonstrated in a number of cases.

The concentration of boric acid solutions by the passage of electrical current through an electrolytic cell with three compartments separated by ion exchange membranes (one cation exchange—MK40, and one anion exchange—MA40) has been investigated.[338] In order to decrease the cell resistance the cathode compartment contained potassium chloride, the anode compartment magnesium sulphate or sulphuric acid, and the central compartment was packed with the cation-exchange resin KU-2. Recirculation of anolyte and central compartment solution (the experimental solution containing boric acid) was also used. Apparent current efficiencies in excess of 100% suggest that a polymeric ion containing more than one boron per unit charge is being transported. The effect of pH on transport in a similar cell (five compartments with IRA-120 or IRA-400 membranes) showed a maximum transport at pH 11.[339]

MISCELLANEOUS REACTIONS OF BORIC ACID

The interaction of boric acid solutions with the corrosion products of nickel–chromium steels has been investigated[341–2]; boron is absorbed into oxidic corrosion products, including corrosion films, in a reversible equilibrium of uncertain type. The action of boric acid on aluminium surfaces has also been studied[343]; it appears that boron is incorporated into the surface to aid in preventing further corrosion.

The effect of boric acid on the thermal decomposition of metal perchlorates has been studied[344]; it is suggested that the decomposition is accelerated through formation of the metal borate and perchloric acid. The direct reaction of boric acid (or boric oxide or metal borates) with hydrogen in the presence of aluminium halides above 100°C is claimed to produce high-purity diborane.[345]

Boric acid is known to form compounds with many leather tanning substances, such as quebracho, tannin, catechin, etc.[346] Gels useful in cosmetics and pharmaceuticals are claimed from the reaction of boric acid (or borax) with aqueous solutions of $Al(OH)_xCl_{3-x}$ such that the final atomic ratios are 7–5 Al, 3 Cl, and 0·65–3·7 B.[347]

Boric acid is claimed to react with organic isocyanates,[348] and di-isocyanates[349]; in the latter instance polymeric materials are obtained. It also reacts with polysiloxane materials to form 'bouncing putties' of various types; examples are discussed in references 350 and 351. A resinous material useful for impregnating porous materials is claimed from the reaction of boric acid with dicyandiamide and formaldehyde.[352]

The exchange of heavy oxygen between water and boric acid is rapid at 100°C.[353]

Boric acid forms coloured complexes with many organic dyes, which can be used in analytical procedures for boron or for the dye itself. Examples of these complexes and their absorption spectra are provided in references.[353–8]

Boric acid (glass) serves as an excellent base for phosphors, in that many different organic molecules can be dissolved in the melt at relatively low temperatures without decomposition; the resulting solid solutions (after cooling) show fluorescence under activation with ultra-violet light. Kasha[376] has provided directions for the preparation of suitable specimens for optical research. Neelakantam and co-workers[377–81] have examined many organic compounds of differing types in a study of factors affecting wavelength, intensity, and duration of phosphorescence. Typical examples are presented in Table LIX. Additional studies have been made by other workers, see for example references 382–6. Although there is some evidence for reaction between boric acid and some of the added organic molecules, it is not a necessary condition for fluorescence or phosphorescence. The fluorescence of the products of the reaction of boric acid with some of the added molecules in sulphuric or phosphoric acid solution has been used as a sensitive analytical detection method for boron.[377–9, 385] It has been suggested that the fluorescence upon reaction with boric acid represents a positive test for the presence of a hydroxyl group *ortho* to a carbonyl group in aromatic compounds, although the lack of such fluorescence does not prove the absence of such a grouping.[378] The observed fluorescence is a function of the added organic molecule, and is not observed in pure boric acid. It is due to triplet–singlet transitions[388–90] of the organic molecule; in many cases the triplet state has a long lifetime in boric acid glass, and direct study of the properties of this state can be made by virtue of the phosphorescence saturation phenomenon,[391] such as direct determination of the magnetic susceptibility.[392]

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SECTION A7

PRODUCTION OF BORIC ACIDS

BY D. L. PERRYER

The two boric acids of commerce are orthoboric acid, H_3BO_3, and metaboric acid, HBO_2. The former, more often referred to simply as boric acid, is encountered far more frequently in industry and is produced at a rate of over 200,000 tons annually, which is at least a thousand-fold greater scale than the latter. Much orthoboric acid is, however, first dehydrated to the metaboric acid stage *in situ* in connection with air oxidation of hydrocarbons.

ORTHOBORIC ACID

Laboratory Preparation

Boric acid is readily prepared by acidifying a hot concentrated solution of borax.[5]

$$Na_2B_4O_7,10H_2O + H_2SO_4 \rightarrow 4H_3BO_3 + Na_2SO_4 + 5H_2O$$

The boric acid can be recovered by filtering it from the sodium sulphate liquor. It can also be prepared by reaction of a mineral acid with one of the insoluble borates.[1] For example, a hot suspension of ground colemanite in water when treated with sulphuric acid gives calcium sulphate and boric acid:

$$2CaO,3B_2O_3,5H_2O + 2H_2SO_4 + 6H_2O \rightarrow \underset{\text{Gypsum}}{2CaSO_4,2H_2O} + 6H_3BO_3$$

By filtering off the gypsum while the reaction mixture is still hot and cooling the filtrate, boric acid is obtained in good yield.

Industrial Production

Boric acid is obtained industrially from the naturally occurring acid contained in various fumaroles, particularly the 'soffioni' at Lardarello in Italy, and from borate minerals and brines by chemical reaction.

FROM FUMAROLES OR 'SOFFIONI'

The quantity of commercial boric acid made from natural fumaroles is relatively small; it was about 2000 tons/year in 1950.[2] Besides boric acid, which is present at a concentration of 0·35 g kg^{-1} vapour, there are other materials of commercial interest, in particular carbon dioxide, ammonia and the inert gases helium, argon and neon.[2] The steam is used directly in turbines for power generation and is then condensed to give a solution containing 0·4–0·5% of boric acid and 0·1–0·3% by weight of ammonia. Evaporation using low-pressure steam produces boric acid crystals which, after centrifuging and drying, have a purity of 95–97%.[3] A method of extracting boric acid from the steam using a soap or oil emulsion which does not absorb other constituents has been proposed.[4] The borate emulsion is acidified, washed with a sodium salt solution to extract the boric acid, re-saponified and re-cycled.

There are published a number of reviews on the early history of boric acid production from Italian soffioni.[5–7]

FROM BORATE MINERALS

Relatively few of the large number of borate minerals are significant in the production of boric acid. The most important for industrial requirements are mainly those of the alkali and alkaline-earth metals and include borax ($Na_2O,2B_2O_3,10H_2O$), kernite ($Na_2O,2B_2O_3,4H_2O$), ascharite ($2MgO,B_2O_3,H_2O$), colemanite ($2CaO,3B_2O_3,5H_2O$), ulexite ($Na_2O,2CaO,5B_2O_3,16H_2O$) and hydroboracite ($CaO,MgO,3B_2O_3,6H_2O$).

Sodium Ores

Boric acid is produced from the sodium borates using sulphuric acid, giving sodium sulphate as a by-product. This is recovered from solution either as the decahydrate[8], which can then be dehydrated in a calciner, or directly as the anhydrous salt.[9] The unusual solubility characteristics of sodium sulphate, which is more soluble at higher than at lower temperatures[10], permit these alternative methods of separating the sulphate. To produce the decahydrate, borax is dissolved in sodium sulphate mother liquor in a cyclic process and treated with sulphuric acid at 40–45°C. On cooling this solution deposits boric acid, which is then separated by standard techniques. Addition of more borax at this stage, followed by further cooling, causes the sodium sulphate decahydrate to crystallize.[8] The mother liquor is re-cycled to the first stage. Phase diagrams[11] of the system Na_2SO_4–$Na_2B_4O_7$–H_3BO_3–H_2O at 20·5°C, 23·5°C and 28·5°C help to explain this technique.

Anhydrous sulphate can be obtained by carrying out the reaction at an elevated temperature.[9, 12] Borax and sulphuric acid are added at 50°C to a re-cycled boric acid mother liquor which is saturated at 95°C with respect to sodium sulphate and at 30°C with respect to boric acid. The solution is then heated to 95°C so that the solubility of sodium sulphate is exceeded, but that of boric acid is just below saturation. This results in the precipitation of anhydrous sodium sulphate, which is separated. On cooling the mother liquor, boric acid crystallizes out while sodium sulphate remains in solution. After separation of the boric acid, the resulting mother liquor is re-cycled to the first stage of the process. Because of the gain in water content due to the chemical reaction, crystallization of boric acid is usually carried out by air cooling or in vacuum crystallizers so that the excess of water in the liquors is removed.[12]

Techniques for producing boric acid directly from crude borax ores containing about 25% of B_2O_3 (borax contains 36·5% of B_2O_3) have been proposed.[13–15] The presence of ferric iron in the liquors, which is dissolved from the gangue constituents of the ore, tends to inhibit the precipitation of anhydrous sodium sulphate and thus hinders the correct operation of the process. The removal of the ferric iron by addition of alkali to convert the iron to the hydroxide, addition of sodium thiocyanate, or use of a reducing agent such as sulphur dioxide can restore conditions such that sodium sulphate is no longer present as a supersaturated solution.[16] For iron concentrations of 100 p.p.m., for example, addition of about 3 lb of sulphur dioxide per 5000 U.S. gal of solution is sufficient to reduce all the iron to the ferrous state.

Boric acid can be obtained directly in the solid form by the reaction of borax suspended in cold water with sulphuric acid, the amount of water present being just sufficient to dissolve the sodium sulphate thus formed, but insufficient to dissolve either the borax or the boric acid.[17–18] Potassium pentaborate can be substituted for borax in the reaction with sulphuric acid[19], giving potassium sulphate as a by-product by evaporation of the mother liquors, which are then re-cycled.

Other acids such as nitric acid[20], phosphoric acid[21] and sulphur dioxide[22] can be used to obtain boric acid from borax, giving as by-products sodium nitrate, $NaNO_3$, sodium dihydrogen phosphate, NaH_2PO_4 and sodium bisulphite, $NaHSO_3$, respectively.

Ammonium sulphate can replace sulphuric acid in the reaction with borax[23] forming ammonia as a by-product.

The use of carbon dioxide has been suggested as a means of decomposing borax to give boric acid.[24] Sodium bicarbonate is produced as a by-product, and the reaction must be carried out under pressure to increase the solubility of the carbon dioxide and to cause a favourable shift in the equilibrium reaction shown below. Starting with sodium tetraborate pentahydrate, the chemical reaction is expressed by the equation:

$$Na_2B_4O_7,5H_2O+2CO_2+2H_2O \rightleftharpoons 2NaHCO_3+4H_3BO_3$$

By using the appropriate mixture of borax decahydrate and pentahydrate, the need to add or remove water in the process is avoided. In cyclic processes, which are more convenient for commercial use, temperatures between 25° and 75°C and pressures between 30 and 615 lb in^{-2} (abs.) can be used. The success of the process depends on application of the Na_2O–B_2O_3–CO_2–H_2O phase diagram at various temperatures and pressures. Empirical formulae[24] can be used to calculate the reagent concentrations, temperature and pressure of carbon dioxide for a particular mother liquor. In a typical cycle 4·18 lb of borax pentahydrate are added to a boric acid mother liquor containing 3·74 lb of Na_2O, 11·8 lb of B_2O_3 and 82·2 lb of H_2O at 32°C and under a carbon dioxide pressure of 48 lb in^{-2} (abs.). The resulting solution is heated to 45·7°C and the carbon dioxide pressure increased to 615 lb in^{-2} (abs.). Sodium bicarbonate precipitates at this point and is removed by filtration. The crystals are washed with 0·25 lb of water and the washings added to the filtrate. Boric acid is then crystallized from solution by cooling the filtrate to 32°C and by releasing the carbon dioxide pressure to 48 lb in^{-2} (abs.). After washing the boric acid crystals with 0·26 lb of water, which is added to the filtrate, the cycle is repeated. The boric acid yield is 3·55 lb per 100 lb of boric acid mother-liquor per cycle.

Ion-exchange resins can be used for the production of boric acid from sodium borates, and although strongly acidic resins having SO_3H groups as the exchange sites are satisfactory, weakly acidic cationic exchange resins having carboxylic groups as the ion exchanging media[25] are preferable since they can be regenerated with almost quantitative efficiency. A concentrated solution of borax in re-cycled boric acid mother-liquor is first passed through the ion-exchange resin in its acid form at about 80°C. Sodium is removed almost quantitatively. The resultant boric acid solution is cooled to 20–30°C; boric acid crystallizes and is removed to give a 97% yield. The boric acid mother-liquor is recycled. Regeneration of the resin to convert it back from the sodium into the acid form with re-cycled sodium sulphate mother-liquor containing 10% sulphuric acid is then carried out, also at 80°C. The resultant liquor is cooled to crystallize sodium sulphate in 65% yield. The sulphate is separated and the mother-liquor is re-cycled. An advantage of this method is that boric acid is crystallized from liquors almost free from sulphate and can be obtained sufficiently pure for commercial use directly without the need for recrystallization.

Electrodialysis has also been proposed for boric acid production.[26, 27] A borax solution is placed in the anode compartment and a mineral acid, such as sulphuric acid, in the cathode compartment. The two solutions are separated by a commercial semi-permeable membrane which allows the passage of sodium ions only. When a potential difference is applied between the electrodes, sodium ions migrate through the membrane to the cathode compartment, forming sodium sulphate, while the solution in the anode compartment becomes progressively more concentrated in boric acid. A continuous process can be developed, although the maximum temperature is limited to about 50°C to avoid deterioration of the membrane. The process is more efficient when the sodium salt of a strong acid, for example, sodium sulphate, is placed in the anode compartment with the borax. Similarly, a strong acid such as sulphuric acid placed in the cathode compartment ensures high conductivity and allows complete decomposition of the borax.

Sodium Borate Brines

The chief commercial source of boron compounds in the form of brine is Searle's Lake in California, U.S.A.[28] Borax is present in the brines at concentrations of about 1·5% by weight together with variable quantities of numerous other salts, the chief of which are sodium chloride (16·5%), sodium sulphate (6·8%), potassium chloride (4·8%), sodium carbonate (4·8%) and sodium phosphate (0·16%).[11] Smaller quantities of sodium iodide and bromide and lithium chloride are among the other salts present.

The basic problem is the initial isolation of borax from the brines before conversion by standard techniques to boric acid. Although there are only two soluble metallic cations and four anions of any significance, the complex nature of the brine means that a considerable number of multi-component phase equilibria had to be evaluated before an economic process could be designed and operated.[11]

The process for producing borax started in 1916, and was improved in 1921 as a result of research on phase equilibria. However, boric acid was not produced until 1927.[28] In the original process brine was pumped from wells and concentrated in triple-effect evaporators.[29] Various salts, mainly sodium chloride, sodium carbonate and burkeite ($2Na_2SO_4,Na_2CO_3$) separate and are removed by classification in a continuous separator. The concentrated liquor, free from solids, is then cooled rapidly to crystallize potassium chloride, which is removed leaving a supersaturated borax solution. This is seeded and cooled to produce sodium borate pentahydrate, which in turn is recrystallized to produce either penta- or decahydrate, part of which is used to feed the boric acid plant.

A later modification involved carbonation of the lower strata brines to produce further quantities of borax and sodium carbonate.[29]

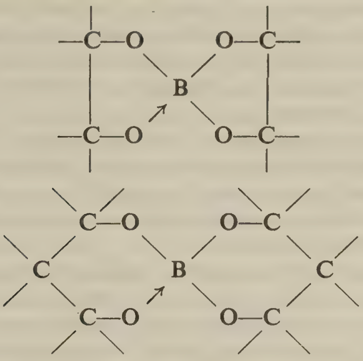
In 1962, a new process using liquid–liquid extraction for separating borax from the brines was started. This involves the use of an organic polyol as the extractant.[30] Although early work had been directed at the recovery of borates by extraction with alcohol[31], only isoamyl alcohol[32–3] and fusel oil[33] had previously shown any promise and these had low distribution coefficients. Diethylene glycol has also been suggested as a solvent.[34] The discovery that aliphatic polyols such as 1,2-octane diol, 2-ethyl-1,3-hexane diol and 1,2,6 hexane triol have specific selectivity for boron compounds[35] was a significant advance. Extraction of a solution containing 1·2% of borax and a variety of other salts with an equal volume of a 50:50 mixture of 2-ethyl-1,3-hexane diol and ether gave the results shown in Table I.

Later developments in polyol synthesis have shown that aromatic polyols have extraction coefficients in the range 50 to 100.[30, 36–7]

Table I

Salt	Concentration in aqueous solution, %, before extraction	Concentration after extraction	
		% in aqueous solution	% in organic phase
NaCl	19·04	19·49	0·06
Na_2SO_4	6·03	—	0·00
Na_2CO_3	3·78	3·70	0·07
$Na_2B_4O_7$	1·19	0·17	2·50
Wt-% $Na_2B_4O_7$ of total solids	3·96	—	95·1
$Na_2B_4O_7$ distribution coefficient	—	14·7	

The selective action of the polyol on the borate is believed to be due to the formation of 5- or 6-membered rings with the boron atom as follows[37]:



The organic extract is acidified with dilute sulphuric acid, giving boric acid, sodium sulphate and the regenerated extractant which is recycled to the extraction stage. After evaporation, the liquor is cooled and boric acid is crystallized; further cooling produces sodium sulphate.

Calcium Ores

When sulphuric acid is added to colemanite ($2CaO,3B_2O_3,5H_2O$) or pandermite ($4CaO,5B_2O_3,7H_2O$), the by-product is insoluble calcium sulphate[5] in the form of gypsum:

$$4CaO,5B_2O_3,7H_2O + 4H_2SO_4 + aq. = 4CaSO_4,2H_2O + 10H_3BO_3 + aq.$$

The mixed mineral ulexite $Na_2O,2CaO,5B_2O_3,16H_2O$ reacts with sulphuric acid to form sodium sulphate and gypsum[38] as waste products.

The reaction with these minerals is normally carried out hot (80–90°C) by first grinding the mineral, mixing with re-cycled mother-liquor, heating, and adding concentrated sulphuric acid. After filtering off the gypsum, the hot liquor is cooled to crystallize boric acid, which is removed by centrifuging. The mother liquor is then re-cycled. With ulexite, removal of sodium sulphate is necessary either by evaporation and crystallization, or by discarding some of the mother liquor. Boric acid obtained from ulexite is contaminated with sodium sulphate and has to be either thoroughly washed or recrystallized.

Although decomposition with sulphuric acid is still the commonest technique employed for the production of boric acid from the calcium borates, various other methods have been proposed. Thus sulphur dioxide has been suggested as an alternative to sulphuric acid. By bubbling this gas through a suspension of ground ore in water[39–41] calcium sulphite is precipitated and can be filtered off before crystallizing the boric acid. An ingenious technique using the variation of solubility of boric acid in the system Na_2O–B_2O_3–H_2O has been suggested.[42–3] Ground colemanite is suspended in a solution saturated with boric acid and containing sodium sulphite in such quantity that the molar ratio $B_2O_3:Na_2O$ is 3:1. Reaction takes place with the colemanite forming calcium sulphite and sodium borate. The calcium sulphite is filtered off and discarded. Boric acid remains in solution in the filtrate since the $B_2O_3:Na_2O$ ratio is increased to 6, which is at a high point in the solubility curve for boric acid in the presence of sodium in solution. The filtrate is treated with sulphur dioxide, which reacts with the sodium borate to form sodium sulphite, bisulphite and boric acid. The boric acid is precipitated and removed by normal methods, and the mother-liquor is recycled. One advantage of this process is that it can be conducted at ambient temperatures.

Hydrochloric acid[44–5], phosphoric acid[46] and nitric acid[47] have all been suggested as alternative reactants for decomposing calcium borates to form boric acid and the corresponding calcium acid salt.

The action of cation-exchange resins on calcium borates by suspending the ground mineral in water and adding the appropriate quantity of resin in the H^+ form[48] has been proposed. Exchange of the calcium ions for hydrogen ions leads to the formation of boric acid and the calcium form of the resin, which is then regenerated with strong mineral acid.

Electrolysis can also be applied to insoluble borates[49] by mixing them with a soluble salt such as calcium chloride or sodium sulphate to form an electrolyte, heating to 95°C and passing a current between an iron cathode and carbon anode. Boric acid collects in the anode compartment, the contents of which are filtered and cooled to produce the boric acid.

Apart from the use of sulphuric acid, perhaps the most important alternative commercial method employs ammonia and carbon dioxide. Garbato, Giorgini and Nencetti[50–1], who give a useful bibliography, treat finely ground colemanite with a solution of ammonia and carbon dioxide. After completion of the reaction, the resulting calcium carbonate is removed by filtration and the solution is boiled to decompose the ammonium borate formed. The process proceeds according to the following reactions:

$$2CaO,3B_2O_3,5H_2O + 6NH_3 + 2CO_2 + 4H_2O \rightarrow 2CaCO_3 + 6NH_4H_2BO_3$$
$$6NH_4H_2BO_3 \text{ boiling} \rightarrow 6NH_3 + 6H_3BO_3$$

Best results were obtained by calcining ground colemanite at 500°C to give a fine mineral (92% passing 200 mesh) and treating this at 55°C with a mother-liquor containing a 22% excess of ammonia and a 72% excess of carbon dioxide with respect to stoicheiometric quantities. Decomposition of the ammonium borate by distilling the solution followed by cooling the resultant liquors gives boric acid in 97% yield. In this process only carbon dioxide is consumed. Most of the ammonia can be recovered and re-cycled.

In May and Levasheff's process[52] ammonium borate is crystallized from solution and calcined to remove the ammonia. Ammonium sulphate can also be used to decompose colemanite[53] by reaction at 95–105°C to form calcium sulphate, ammonia and ammonium pentaborate. The pentaborate is reacted with ammonium bisulphate to form boric acid and ammonium sulphate, which is re-cycled. Carbon dioxide and ammonia are used to convert the calcium sulphate to calcium carbonate and ammonium sulphate. Calcination of the ammonium sulphate gives the bisulphate used in the decomposition of ammonium pentaborate and ammonia, which is recovered.

Alternatively, the solution of ammonium borates formed by the initial reaction between ammonium sulphate and colemanite can be treated either with carbon dioxide or sulphur dioxide, after filtering off the calcium sulphate, to precipitate boric acid.[54] The use of ammonium sulphate is unlikely to be as attractive commercially as the direct use of ammonia and carbon dioxide because of the additional processing steps involved.

Carbon dioxide itself has been proposed for the decomposition of colemanite[55–6, 139], pandermite[56], inyoite[56] and hydroboracite.[56] By heating a mixture of colemanite (80 parts) and silica (32·2 parts) in the presence of water to 260°C with carbon dioxide under pressure, boric acid is formed in high yield together with calcium carbonate.[55] 90–92% of the boric acid can be extracted by heating the finely ground mineral (minus 60 mesh) with water and 30% carbon dioxide to 100°C and 15 atm for 1·3 h. The filtrate is acidified and cooled to yield boric acid.[56] Decomposition of minerals containing only 10% of B_2O_3 and calcareous dolomite by first calcining the mineral to *ca.* 1100°C followed by treating it in aqueous suspension at 20–50°C with carbon dioxide has been found an effective method of producing boric acid[57], although calcination at a lower temperature (500–550°C) is said to be just as effective.[58]

Magnesium Ores

The decomposition of ores containing magnesium, such as ascharite ($2MgO,B_2O_3,H_2O$) and hydroboracite ($CaO,MgO,3B_2O_3,6H_2O$) with sulphuric acid presents the problem of removing the soluble magnesium sulphate from the reaction circuit while retaining a high yield of boric acid. Because of the high solubility of magnesium sulphate, discarding a proportion of the mother-liquor, with a consequent loss of boric acid, is usually necessary to remove all the magnesium sulphate produced in the reaction. Magnesium ores are plentiful in the Inder region of the U.S.S.R. and provide the raw materials for a large part of the borate industry there. Berlin[59–61] reviews some of the technical problems facing the industry in Russia and suggests that ores containing calcium and magnesium should be treated with 25% less than the theoretical quality of sulphuric acid[62] to get the best results.

A number of methods have been proposed for dealing with the magnesium sulphate produced in the reaction between ores containing magnesium and sulphuric acid. The mother-liquor obtained after crystallizing the boric acid can be concentrated by evaporation and crystals of $MgSO_4,7H_2O$ separate out.[63–4] The concentrated liquor is then re-cycled to the process. Addition of sodium sulphate[65] followed by evaporation causes the magnesium to be removed as a double sodium magnesium sulphate. The addition of magnesium hydroxide or carbonate has also been proposed[66] to facilitate the crystallization of the sulphate.

Batuner[67] studied the phase diagram $H_2O–H_2SO_4–MgSO_4–H_3BO_3$ and found that the solubility of boric acid in the presence of 50% sulphuric acid and magnesium sulphate is almost doubled. He also found that sulphuric acid can salt out magnesium sulphate and added sulphuric acid to the mother-liquor after concentrating it by evaporation. The mother-liquor containing the sulphuric acid used for salting out was then used to decompose the ore after removing magnesium sulphate. Scholle *et al.*[68–9] added sulphuric acid to a mother-liquor nearly saturated with magnesium sulphate, obtained by re-cycling the brine to the reactor. Magnesium sulphate was precipitated by the salting-out effect. After removal of the solids, the liquor was evaporated under vacuum until the acid sulphate of magnesium could be separated. The residual liquor was then recycled to decompose further ore.

Complete separation of boric acid and magnesium sulphate is not possible by crystallization techniques, which result in a loss of up to 15% of the B_2O_3 content of the ore in liquor discarded from the system. For this reason, separation by ion exclusion using strongly basic anion-exchange resins was proposed by Popov and Kononov[70], who give a useful bibliography. Ion exclusion can separate two soluble compounds only if one of them is strongly ionized in solution, as in the case of magnesium sulphate, and the other only slightly ionized, e.g. boric acid. Solutions containing 0·5M-H_3BO_3, 1·6M-$MgSO_4$ and 0·07M-H_2SO_4 could be effectively separated using this technique to give dissolved concentrations higher than those in the original mother-liquor. The use of a flotation agent has also been suggested for separating boric acid.[71–2]

Simultaneous production of fertilizers in conjunction with boric acid is one method of utilizing boron contained in discarded mother liquors. Thus, decomposition of magnesium borate or mixed calcium magnesium borate ores with phosphoric acid[73–5] or mixtures of phosphoric acid and sulphuric acid[74] produces boric acid, calcium phosphate, $Ca(H_2PO_4)_2$, and magnesium phosphate, $Mg(H_2PO_4)_2$, in solution. Neutralization with lime or ammonia precipitates partly soluble phosphates and these can be used to form fertilizers containing phosphorus, boron and magnesium. Alternatively, a mixture of nitric and sulphuric acids can be used.[76] The mother-liquor, after cooling and removing boric acid crystals, can be evaporated to give a fertilizer containing nitrogen and boron or treated with solid potassium chloride to give potassium nitrate by crystallization. Further treatment of the filtrate with lime gives a low grade boron–magnesium fertilizer. This method is claimed to reduce the boric acid losses by two-thirds.

Kurman, Berlin and Katalymov[77] made tests on a variety of low-B_2O_3 content Russian ores, including datolite (B_2O_3 3–8%), tourmaline tailings (B_2O_3 2·5–6%)

and Inder borates (B_2O_3 up to 20–30%) and used the mother-liquors for boron–magnesium fertilizers and for making the mixed ammonium–boron sulphate, $NH_4B(SO_4)_2$. The mother-liquors can also be neutralized with lime[78] or chalk[79] and evaporated to dryness.

The discarded mother-liquor has also been used for preparing thermo-insulating material by mixing it with lime, decanting supernatant liquor and mixing the resultant slurry containing 60–65% moisture with asbestos.[80]

The use of mother-liquors containing magnesium to decompose calcium borates has been proposed.[81] Magnesium sulphate contained in the liquors reacts to form boric acid and calcium sulphate which, it is claimed, is more freely filtered when produced in this way. Treatment of brines or liquors containing boron and magnesium with a saturated solution of lime so that the boron is precipitated with the magnesium hydroxide has been proposed.[82] Further treatment of the boron–magnesium concentrate with lime water in two stages produces a boron-rich concentrate.

Parameters affecting the reaction of sulphuric acid with hydroboracite and ascharite have been studied in some detail by Yakhontova and Kuznetsova[83], who give the effects of temperature, duration of reaction and solid–liquid ratio on the extent of decomposition. The effects of re-cycling the mother-liquor to the reactor were also determined. A bibliography is given.

Zdanovskii and Imamutdinova studied the rates of dissolution of various borates, including inyoite, hydroboracite, ulexite and colemanite in sulphuric and hydrochloric acids.[84–5] The effect of acid concentration was studied and an expression developed in terms of physical parameters for the rate of dissolution.

A method of extracting boric acid from kotoite, a mineral found in Korea having the composition $3MgO,B_2O_3$ and normally occurring mixed with iron oxide and calcium and magnesium carbonate, has been described.[86–7] The mineral is heated with excess of hydrochloric acid to dissolve carbonates, filtered, treated with magnesium carbonate to neutralize excess of acid, again filtered and then cooled to crystallize boric acid.

A 90–93% yield of boric acid can be obtained from ascharite and hydroboracite by treating the ground ore in aqueous suspension with a strongly cationic ion-exchange resin and a small quantity of a sodium salt as catalyst.[88–90] Regeneration of the separated resin with 2N sulphuric acid allows it to be reused. Purity of 99% is claimed by this method.

Cationic resins have also been used for removing magnesium ions from mother-liquors resulting from the reaction between high magnesium-content ores and sulphuric acid.[91] For example, 10 kg of ascharite containing 29·3% of B_2O_3 and 18% of MgO is suspended in hot, re-cycled, treated mother-liquor and concentrated sulphuric acid. Boric acid is crystallized from the cooled solution and the mother-liquor is then passed through a cationic ion-exchange resin to remove magnesium ions. Sixty litres of resin will treat 55 litres of mother-liquor, which is washed through the column with 30 litres of hot and then 15 litres of cold water. The first 12 litres of treated mother-liquor coming from the column are discarded; the rest is re-cycled for a fresh reaction with the ore. The resin is regenerated with 6N-HCl or -H_2SO_4, the eluate being neutralized with magnesite to give a liquor containing 20% of $MgSO_4$.

Ores Containing Silicon

Datolite, $2CaO,2SiO_2,B_2O_3,H_2O$, is the commonest borate ore containing silica and reacts the most readily. Tourmaline, a complex ore containing silica and oxides of sodium, iron, magnesium and aluminium, but only about 3% of B_2O_3, has also been tested.

Datolite is treated with sulphuric acid to form calcium sulphate and boric acid.[92] For an ore containing 4·9% of B_2O_3, 11·66 tons of ore and 2·83 tons of sulphuric acid are required to produce 1 ton of boric acid.[93] Some difficulty is experienced with colloidal silica, and this can be coagulated with organic bases such as pyridine in conjunction with aluminium hydroxide[93–4] or by adding 50–150 g l^{-1} of magnesium or sodium sulphate to the reaction mixture.[95]

Comparative data are given by Schmutzler and Kircheisen[96] for the production of 1 ton of boric acid from datolite, colemanite and ascharite/hydroboracite. Since 9–12 tons of mud result from the production of 1 ton of boric acid from datolite, the economics depend on the effective utilization of this large quantity of waste product.

Datolite can also be ignited at 800–850°C[97], or treated with superheated steam at 950–1200°C[98], and then treated with sulphuric acid, filtered, boiled with limestone to remove heavy metals, and then processed further to give boric acid. Treatment at 850–1100°C with an alkali-metal or alkaline-earth carbonate has also been described.[96, 99]

Boric acid can be obtained from tourmaline by first calcining and then treating it with sulphuric acid, filtering and evaporating the filtrate.[100] Alternatively, it can be mixed with carbon with or without an alkali-metal or alkaline-earth carbonate, fired at 1200°C and then extracted with dilute acid.[101]

Miscellaneous Techniques

Preparation of boric acid by treating hot borax solutions with barium hydroxide to produce barium borate, $Ba(BO_2)_2$, as an intermediate is described.[102] The barium borate is filtered off and then suspended in water in an autoclave at 110°C and treated with carbon dioxide at a pressure of 250 lb in^{-2} (gauge). Ninety-nine per cent conversion to boric acid is claimed.

Conversion of amorphous or crystalline boron to boric acid by photosynthesis has been described by Calcagni.[103] By suspending the boron in very pure water for 7–11 months, boric acid is formed.

Separation of boron compounds from saturated solutions of borax, boric acid and salt by flotation is possible with oleic acid, pyridine and aromatic amines.[104–5] Direct separation of boric acid from the reaction mixture of colemanite with sulphuric acid or sulphur dioxide in solution is possible by flotation without any flotation agent[106]; 90% recovery of boric acid is claimed. The presence of froth-controlling salts such as copper or aluminium sulphate is an advantage.[107]

Recovery of boric acid from brines containing less than 1% in solution can be effectively carried out using magnesium oxide[108] which acts as an absorption agent. The effect of adding salts such as potassium nitrate, magnesium nitrate, calcium chloride, potassium chloride or magnesium chloride on the recovery of boric acid from brines has been shown graphically.[109]

Recovery of boric acid from trimethyl borate can be accomplished by adding a saturated boric acid solution to the methyl borate–methanol azeotrope.[110] After filtering to remove precipitated boric acid, the methanol is distilled off, and the 'bottoms' give more boric acid on cooling, plus a saturated boric acid solution for recycling to the first stage.

Preparation of Pure Boric Acid

Pure boric acid having total impurities in the region of 10–20 p.p.m. or less, compared with the 0·1–1·5% impurities in the technical grade, is usually prepared industrially by one of two methods. Recrystallization of the technical grade from aqueous solution containing a trace of sulphuric acid[111] using deionized water as the solvent, and purification of boric acid solutions by ion exchange are the methods employed. Reduction of the iron content of boric acid to 5×10^{-7} g per g of H_3BO_3 can be accomplished[112] by reducing ferric iron in a saturated boric acid solution with hydroquinone or ascorbic acid at 40–50°C followed by complexing the ferrous ions with 2,2′-bipyridine. The resulting solution when passed through a mixed-bed ion-exchange column gives pure boric acid on crystallization.

The use of three columns of cationic followed by three columns of anionic resin to purify a 4·5% boric acid solution at the rate 30–40 ton day^{-1} is described by Meleshko *et al.*[113-14] The solution is filtered before passing it through the columns. Regeneration of the cationic resin is carried out with N-HCl and the anionic resin with 0·25N-NaOH solution.

Production of pure boric acid from a solution of technical grade borax and boric acid containing the equivalent of 146 g l^{-1} of boric acid has been described.[115] The solution was passed at 100 l min^{-1} through a 1-litre capacity cationic ion-exchange column at 80°C giving a product containing less than 0·05% of Cl^- ions and no SO_4^{2-} ions, in 96–99% yield.

Recovery of Boric Acid from Dilute Solutions

A number of chemical methods have been suggested for removing boric acid from brines and dilute solutions.[116-19] The use of ferric oxide, chromic oxide freshly prepared with sodium hydroxide, or aluminium oxide gels prepared with ammonia solution has been found effective.[116] The presence of sodium silicate or phosphate helps. Regeneration can be achieved by treatment with an alkaline solution followed by rinsing with carbonated water. Gels prepared from lime and aluminium sulphate or a ferric salt have been used[117]; treatment with sulphuric acid or ferric sulphate solution follows to recover the boron. The addition of an alkali to a brine containing both magnesium and boron co-precipitates these materials.[118] Boric acid is released by passing sulphur dioxide through the resulting suspension. A solution containing 14 g of tartaric acid, 42 g of $BaCl_2,2H_2O$ and 100 g of ammonium chloride per litre of water has been used to precipitate boron quantitatively as the borotartrate from solutions containing 0·005% of boron as borates.[119] Sufficient reagent to give a molar ratio of tartrate to borate of 2:1 must be used, and 10% of the reagent volume of concentrated ammonia solution is added just before use.

The use of strongly basic anion-exchange resins has been described, with performance details, by a number of authors.[120-5] Ion-exchange resins are also used in controlling concentration levels of boric acid in water-moderated nuclear reactors.[126-9] A boron-specific ion-exchange resin based on N-methyl-glucamine is described by Kunin and Preuss.[130] The resin is easily regenerated with sulphuric acid solutions. Concentration of boric acid using a cationic resin and cationic and anionic exchange membranes is described by Shubin and Makovskaya[131] for use in the recovery of boric acid from datolite ores. Performance data are given and the economics of the process are discussed.

METABORIC ACID

Laboratory Preparation

Metaboric acid, HBO_2, crystallizes in three monotropic forms, as shown by Kracek, Morey and Merwin[132], who studied the system B_2O_3–H_2O over the whole composition range and gave a phase diagram. These authors showed that the three types are distinguished by different crystal forms, densities and melting points, viz.,

HBO_2 I, rhombic, 2·486 g cm^{-3}, m.p. 236°C;
HBO_2 II, monoclinic, 2·044 g cm^{-3}, m.p. 201°C;
HBO_2 III, orthorhombic, 1·784 g cm^{-3}, m.p. 176°C.

When boric acid is slowly heated, water is lost to produce flaky crystals of the metastable HBO_2 I at a temperature below 130°C. These crystals slowly change to the coarsely crystalline HBO_2 II if the temperature is kept below 150°C. HBO_2 I may be prepared by slowly dehydrating boric acid in a covered flask and then gradually increasing the temperature to 200°C; HBO_2 I crystallizes out and then slowly dissolves.[133]

Crystals of HBO_2 II and HBO_2 III were also observed by Tazaki[134], who does not mention the existence of HBO_2 I. In experiments on the volatility of orthoboric acid in steam, Stackelberg and Quatram[135] found that metaboric acid forms in the vapour phase when the steam pressure is 1 atm. and the temperature 141°C. These authors also claim that polymerization takes place in the solid state to form a chain:

$$\text{—B(OH)O—B(OH)O—}$$

Urosov studied the decomposition of boric acid at various levels of external pressure.[136] Hackspill and Kieffer[137] also describe the dehydration of orthoboric acid and prepared metaboric acid by heating it in a steam current at 135°C. No mention is made by these authors of different monotropic forms.

Industrial Production

Industrially, metaboric acid is prepared by heating orthoboric acid in stirred open steam-heated vessels at about 130°C.[138] HBO_2 III is first formed which on prolonged heating gradually recrystallizes to the coarsely crystalline HBO_2 II. The decomposition stops at this stage unless the temperature is allowed to rise beyond 150°C.

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SECTION A8

SUB-BORIC ACIDS

BY D. NICHOLLS

Distinct from the ortho- and meta-boric acids among compounds which contain only the three elements boron, hydrogen and oxygen, there exist several in which the boron atoms are in formal oxidation states less than $+3$. They include sub-boric and hypo-boric acids. Many of the compounds either have not been named in the literature or have been incorrectly named; for simplicity these compounds, particularly those whose structures are uncertain, will be referred to here by formulae only.

Some of the compounds have been isolated only from the hydrolysis products of magnesium boride. The early work in this field was reviewed (Mellor, V, 39) and more recent work on these particular products is summarized.[1] It will be convenient to discuss first the hydrolysis of magnesium boride and those sub-boric acids which can be obtained only by this route.

Sub-Boric Acids Derived from Magnesium Boride

The hydrolysis of the hypothetical boride Mg_3B_2 has produced a variety of sub-boric acids. When the boride is hydrolyzed at room temperature by either water or dilute acid, the main product[2] is alleged to be a substance of composition $Mg_3B_2(OH)_6$:

$$Mg_3B_2 + 6H_2O \rightarrow Mg_3B_2(OH)_6 + 3H_2$$

If the hydrolysis is carried out slightly below $-10°C$ however a different product[3], $H_3B_2(MgOH)_3$, is formed; this reacts with water at room temperature, liberating hydrogen:

$$H_3B_2(MgOH)_3 + 3H_2O \rightarrow Mg_3B_2(OH)_6 + 3H_2$$

The preparation of sub-boric acids from these compounds is summarized in the scheme shown in Fig. 1.

$H_6B_2O_2$

This acid exists in two forms. The α-form is present in the solution from the hydrolysis of 'pure' magnesium boride. The addition of hydrochloric acid to its solutions causes liberation of hydrogen according to:

$$H_6B_2O_2 \rightarrow H_2B_2O_2 + 2H_2$$

Whilst the free acid has not been isolated, its potassium salt, $K_2H_4B_2O_2$, [which is probably best formulated as $K_2H_2B_2(OH)_2$] was prepared[4] by the action of potassium hydroxide solution on magnesium boride. The β-form of $H_6B_2O_2$ is present in solutions obtained by the hydrolysis of magnesium boride which contains unreacted magnesium and boric oxide as impurities.[4] It differs from the α-form in liberating only one molecule of hydrogen per molecule of $H_6B_2O_2$ on treatment with acid:

$$H_6B_2O_2 \rightarrow H_4B_2O_2 + H_2$$

The potassium salt, β-$K_2H_2B_2(OH)_2$, has been isolated as colourless crystals from the

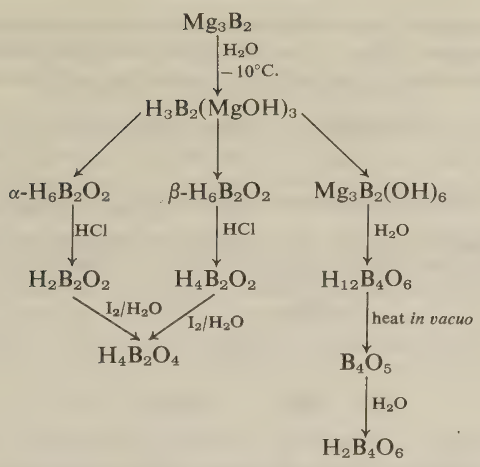


FIG. 1.—Sub-boric acids derived from Mg_3B_2

hydrolysis of a mixture of magnesium boride, magnesium and boric oxide using 0·01N potassium hydroxide.

The salts of both isomers form colourless anhydrous crystals and act as powerful reducing agents. Salts of silver and gold are reduced to the metals. The acids are completely oxidized by nitric acid. The two forms of $H_6B_2O_2$ may be[4] *cis* and *trans* isomers of the anion $[HB(OH)—(HO)BH]^{2-}$.

$H_4B_2O_2$

This acid is formed in solution on acidification of β-$K_2H_2B_2(OH)_2$ with hydrochloric acid. Like $H_6B_2O_2$ it is a powerful reducing agent; with aqueous iodine it is oxidized to tetrahydroxydiboron.[4] The colourless crystalline ammonium salt, $(NH_4)_2B_2(OH)_2$, can be obtained[5] as one product of the fractional crystallization (in an atmosphere of hydrogen) of a solution of $Mg_3B_2(OH)_6$ in concentrated ammonia solution. The crystals are stable in the presence of ammonia solution or below 0°C; when heated *in vacuo* boron monoxide is left as a residue:

$$(NH_4)_2H_2B_2O_2 \rightarrow B_2O_2 + 2H_2 + 2NH_3$$

The potassium salt $K_2B_2(OH)_2$ has also been isolated as colourless crystals.[4]

$H_2B_2O_2$

Aqueous solutions of this acid are obtained by treatment of $K_2H_2B_2(OH)_2$ with hydrochloric acid. They are oxidized by aqueous iodine to tetrahydroxydiboron, $B_2(OH)_4$.[4] The diethyl ester of $H_2B_2O_2$ has been prepared[6] as a dense liquid by reaction of dichloroethoxyborane with sodium amalgam:

$$2B(OC_2H_5)Cl_2 + 4Na \rightarrow (C_2H_5O)B{=}B(OC_2H_5) + 4NaCl$$

$H_{12}B_4O_6$

This acid is known only in solution. It is formed when $Mg_3B_2(OH)_6$ is hydrolyzed by aqueous ammonia. When its solution is evaporated *in vacuo*, the colourless oxide B_4O_5 [1] is left as a residue.

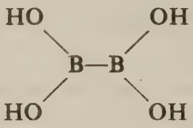
$H_2B_4O_6$

The white oxide B_4O_5 dissolves in water to form a new compound $H_2B_4O_6$.[1] The water-soluble and crystalline ammonium salt, $(NH_4)_2B_4O_6$, is one of the products[5] of the treatment of $Mg_3B_2(OH)_6$ with concentrated aqueous ammonia. It does not yield hydrogen from acids but gives white precipitates with calcium, barium and magnesium salts—a reaction distinguishing it from $(NH_4)_2B_2(OH)_2$. On thermal decomposition in vacuum, the ammonium salt yields B_4O_5:

$$(NH_4)_2B_4O_6 \rightarrow B_4O_5 + H_2O + 2NH_3$$

Tetrahydroxydiboron, Hypoboric Acid, $H_4B_2O_4$

Tetrahydroxydiboron, I, is the most frequently reported of the sub-boric acids and consequently is often called simply sub- or hypo-boric acid:



I

It is formed as a white microcrystalline solid by the action of water on boron monoxide:

$$B_2O_2 + 2H_2O \rightarrow B_2(OH)_4$$

and by the oxidation of aqueous $H_2B_2O_2$ and $H_4B_2O_2$ with iodine. The most convenient preparative routes however involve the hydrolysis of diboron compounds of the type B_2X_4, where X = halogen. Thus diboron tetrachloride is quantitatively hydrolyzed by water vapour at room temperature[7, 8]:

$$B_2Cl_4 + 4H_2O \rightarrow B_2(OH)_4 + 4HCl$$

Whilst diboron tetrachloride is difficult to prepare and handle, tetramethoxydiboron can be prepared readily by the sequence:

$$BCl_3 + 2B(OCH_3)_3 \rightarrow 3B(OCH_3)_2Cl$$

$$2B(OCH_3)_2Cl + 2Na \rightarrow B_2(OCH_3)_4 + 2NaCl$$

When it is hydrolyzed, tetrahydroxydiboron is obtained in approximately 80% yield[6, 9, 10]; the loss of product is due to some B—B bond cleavage with consequent formation of boric acid and hydrogen. The aqueous hydrolyses of tetraethoxy- and tetra*iso*-propoxy-diboron at 0°C however give $B_2(OH)_4$ quantitatively[9]; these esters are readily available[11] from the reactions of the appropriate alcohols on the tetrakisdimethylamide, $B_2(NMe_2)_4$, in the presence of hydrogen chloride at -78°C. Hydrolysis of $B_2(NMe_2)_4$ with hydrochloric acid at 0°C gives only moderate yields of $B_2(OH)_4$.[9, 12]

The standard enthalpy of formation of $B_2(OH)_4$ has been determined[13] by solution calorimetry and found to be $\Delta H_f^0 = -1400 \pm 8$ kJ mole^{-1} ($-335{\cdot}1 \pm 2{\cdot}0$ kcal mole^{-1}). By assuming that the enthalpy of sublimation of $B_2(OH)_4$ is equal to that of boric acid, the energy of the B—B bond in $B_2(OH)_4$ can be calculated to be 351 ± 21 kJ mole^{-1} (84 ± 5 kcal mole^{-1}).

The infra-red spectra of $B_2(OH)_4$ and $B_2(OD)_4$ have been measured[14] over the range 400–4000 cm^{-1}. The vibrational frequency of the B—B bond occurs at 1150 cm^{-1}; other peaks and assignments are 575 cm^{-1} (O—B—O deformation), 1320 cm^{-1} (B—O stretching), 790 and 875 cm^{-1} (B—OH deformations).

Tetrahydroxydiboron is soluble in water and methanol. Its acidity is comparable with that of boric acid and like the latter it forms a complex with mannitol in which there is one hydrogen atom which can be titrated with sodium hydroxide. It can therefore be estimated[15] by direct titration with alkali; indeed it can be estimated in admixture with boric acid simply by performing the caustic soda titration before and after oxidation of the hypoboric acid. The magnesium and barium salts of hypoboric acid, $Mg_2B_2O_4$ and $Ba_2B_2O_4$, can be crystallized[5] from the solutions of the metal hydroxides in aqueous hypoboric acid. On oxidation, tetrahydroxdiboron yields two molecules of boric acid:

$$2B_2(OH)_4 + 2H_2O + O_2 \rightarrow 4B(OH)_3$$

Oxidizing agents capable of bringing about this oxidation include hydrogen peroxide, permanganate, silver(I) and cerium(IV). Oxidation with molecular oxygen occurs rapidly in alkaline solution. The reduction of silver ions may be used as an analytical method since the reaction:

$$2Ag^+ + B_2(OH)_4 + 2H_2O \rightarrow 2Ag + 2B(OH)_3 + 2H^+$$

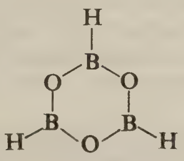
proceeds with quantitative precipitation of metallic silver. The hydrolysis of $B_2(OH)_4$ is typical of B—B species. At 25°C in water very little hydrogen is evolved[9]; in the absence of oxygen and in strongly alkaline solution, quantitative fission of the B—B bond occurs[16]:

$$2OH^- + B_2O_4^{4-} \rightarrow 2BO_3^{3-} + H_2$$

The measurement of hydrogen evolution is also useful in determining hypoboric acid in a mixture of hypoboric and boric acids, or boron monoxide in admixture with boric oxide.

Boroxine, $H_3B_3O_3$

Whilst substituted boroxines have been known for some time, e.g. $B_3O_3(CH_3)_3$ [17] and $B_3O_3Cl_3$ [18], the parent boroxine, II, has been isolated[19] and studied only since 1963.



II

Boroxine is formed as a gas in the reactions of hydrogen with mixtures of boric oxide and boron[19]:

$$3H_2 + 2B + 2B_2O_3 \rightarrow 2H_3B_3O_3$$

or boric oxide and carbon[16, 20] at temperatures in the range 1000–1500°C. It can be condensed to a white solid at −196°C, but when warmed to room temperature decomposition begins; diborane is evolved and boric oxide remains:

$$2H_3B_3O_3 \rightarrow B_2H_6 + 2B_2O_3$$

Boroxine is thus an important intermediate in the synthesis of diborane from boric oxide, carbon and hydrogen.[16] The high-temperature reaction between water vapour and boron also produces boroxine:

$$6H_2O + 6B \rightarrow 2H_3B_3O_3 + 3H_2$$

Alternative routes to boroxine involve the partial oxidation of boron hydrides. Thus boroxine is formed as an intermediate in the reaction of pentaborane-9 with oxygen[21–2]; the precursor of boroxine in this reaction is probably[23] HBO or H_2BOH. The solids produced in the reaction act as catalysts to accelerate the rate of decomposition of the boroxine formed. A simplified preparation of boroxine, starting from diborane, has been described.[24] The reaction between diborane and oxygen is initiated by an electric discharge. Best yields of boroxine are obtained using a 1:1 mole ratio of diborane and oxygen; the reaction stoicheiometry is approximately:

$$B_2H_6 + O_2 \rightarrow 0{\cdot}32H_3B_3O_3 + 2{\cdot}8H_2 + 0{\cdot}4B_2O_3$$

If oxygen is in excess, oxidation to boric oxide occurs: with diborane in excess, the decomposition of the boron hydride becomes important since the pyrolysis is more rapid than the oxidation.

Structural studies on boroxine have been limited to infra-red and thermochemical methods. The infra-red spectrum of solid boroxine[25] measured as a film at −150°C may be interpreted on the basis of the six-membered ring structure characteristic of boroxine derivatives, although the appearance of more than one terminal B—H stretching frequency in the 2500–2600 cm^{-1} region may be due to the fact that the atoms in the ring are non-coplanar. The infra-red spectrum of gaseous boroxine[22, 26] has been measured at room temperature in presence of excess argon, which decreases the rate of decomposition of the boroxine. The spectrum is similar to that of the isoelectronic molecule borazine and is consistent with a planar D_{3h} structure.

Thermochemical data for the reaction:

$$\tfrac{3}{2}H_2(g)+B+B_2O_3 \rightarrow H_3B_3O_3(g)$$

have been determined over the temperature range 1290–1481K using a mass-spectrometric technique.[19] The heats of formation of solid and gaseous boroxine at 298K have been evaluated[27–8]; more recent workers estimate these heats of formation to be −1261±10 (−301·7±2·5) and −1216±8 kJ $mole^{-1}$ (−291·0±2·0 kcal $mole^{-1}$) respectively.

Gaseous boroxine produced in the high temperature reactions is thermodynamically unstable with respect to $B_2H_6(g)$ and $B_2O_3(s)$ at room temperature; $B_3O_3H_3$ molecules produced at high temperatures do, however, show kinetic stability at room temperature. Evaporation of solid boroxine does not produce boroxine gas in any significant amount; diborane is evolved only slowly below 0°C but rapidly above 15°C. When reactions are carried out with solid boroxine at room temperature the diborane produced by the decomposition must be removed by evacuation immediately prior to the reaction.

The reaction of gaseous boroxine with oxygen at room temperature produces a new species, $H_2B_2O_3$.[26, 29] Using infra-red absorption techniques it has been shown that the reaction:

$$H_3B_3O_3(g)+\tfrac{1}{2}O_2(g) \rightarrow H_2B_2O_3(g)+\tfrac{1}{3}B_2O_3(s)+\tfrac{1}{6}B_2H_6(g)$$

is first-order in $H_3B_3O_3$ pressure and approximately zero-order in oxygen pressure. The rate of the reaction is accelerated in vessels coated with solid boric oxide. When $^{18}O_2$ is used as the reactant, the product is mostly $H_2B_2{}^{16}O^{18}O_2$ indicating that the reactant oxygen molecule is retained in the product.[29] This fact is consistent with the proposed mechanism[30] for this reaction which involves the slow formation of $H_2B_2O_3$:

$$H_3B_3O_3(g)+O_2(\textit{on } B_2O_3 \textit{ surface}) \xrightarrow{\text{slow}} H_2B_2O_3(g)+HBO_2(\textit{adsorbed})$$

and the fast decomposition of the species HBO_2. Boroxine reacts with carbon monoxide to yield borane carbonyl[31]:

$$H_3B_3O_3(g)+CO(g) \rightarrow BH_3CO(g)+B_2O_3(s)$$

This reaction can be used as a convenient preparative route to borane carbonyl. The high temperature boroxine is condensed to a solid which is then maintained at −29°C while carbon monoxide is admitted; the mixture is then warmed to room temperature and borane carbonyl is evolved. The kinetics of this reaction have been studied.[30] The rate of reaction is very fast compared with that between diborane and carbon monoxide at low pressures. The reaction of solid boroxine with carbon monoxide may occur via a surface active BH_3 species which is formed in the initial stages of decomposition of the boroxine. The addition of carbon monoxide then results in rapid formation of borane carbonyl via the reactions:

$$H_3B_3O_3(g) \rightarrow B_2O_3(s) + BH_3(surface)$$

$$BH_3(surface) + CO(g) \rightarrow BH_3CO(g)$$

This mechanism accounts for the formation of diborane as a decomposition product of boroxine:

$$2BH_3(surface) \rightarrow B_2H_6(g)$$

The formation of borane carbonyl in the reactions of hydrogen with B_2O_3–C and B_4C–TiO_2 mixtures[16] at temperatures above 900°C is thus accounted for, since both boroxine and carbon monoxide are produced in these reactions. Phosphorus trifluoride reacts with gaseous boroxine[32] at room temperature in a manner exactly analogous to carbon monoxide:

$$H_3B_3O_3(g) + PF_3(g) \rightarrow BH_3PF_3(g) + B_2O_3(s)$$

Kinetic studies indicate that the rate-determining step in this reaction is the slow decomposition of boroxine, the phosphorus trifluoride then reacting on the surface as in the carbon monoxide reaction.

Boroxine undergoes substitution reactions with hydrogen chloride. When the reaction is carried out with gaseous boroxine at temperatures in the range 1090–1150K, mono-$B_3O_3H_2Cl$, di-, $B_3O_3HCl_2$ and trichloroboroxine $B_3O_3Cl_3$ are produced.[28] If a large excess of hydrogen chloride is used, boron trichloride is also formed as a product. These reactions have been studied mass-spectrometrically and thermochemical data for the reaction:

$$B_3O_3H_3(g) + nHCl(g) \rightarrow B_3O_3H_{3-n}Cl_n(g) + nH_2(g)$$

have been tabulated.[28]

The reactions of boroxine with the boron trihalides have been studied in some detail. With solid boroxine and boron trifluoride at room temperature, HBF_2 is produced; the reaction is more rapid than that between diborane and boron trifluoride at similar temperatures. For the reaction:

$$\tfrac{1}{6}B_2H_6(g) + \tfrac{2}{3}BF_3(g) \rightarrow HBF_2(g)$$

ΔH at $296K = 12{\cdot}5 \pm 2{\cdot}1$ kJ mole^{-1} ($3{\cdot}0 \pm 0{\cdot}5$ kcal mole^{-1}). A possible reaction sequence is[33]:

$$B_3O_3H_3(g) + BF_3(g) \rightarrow B_3O_3H_2F(g) + HBF_2(g)$$

$$B_3O_3H_2F(g) + BF_3(g) \rightarrow B_3O_3HF_2(g) + HBF_2(g)$$

$$B_3O_3HF_2(g) \rightarrow HBF_2(g) + B_2O_3(s)$$

Boron tribromide reacts with solid boroxine in a slightly different manner. The product formed at room temperature is B_2H_5Br, but at 100°C $HBBr_2$ is obtained in good yield.[34] Low-pressure reactions of gaseous boroxine with boron trihalides produce the dihalogenoborane and boric oxide.[34] These reactions have been studied kinetically using infra-red absorption techniques. The reactions are approximate to first-order in boroxine pressures and reaction rates increase in the order $BF_3 < BCl_3 < BBr_3$; the reactions are accelerated in cells coated with solid boric oxide. Using ^{10}B-labelled compounds, the spectra of the products show that the boron atoms in $H_3B_3O_3$ appear in HBX_2 and the boron atom in BX_3 appears in B_2O_3. A surface mechanism accounting for the ^{10}B distribution in the products has been proposed.[35]

Hydroxyboroxine, $H_3B_3O_4$

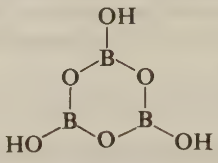
This compound has been observed[19] in small yield in the H_2—B—B_2O_3 system used for preparing boroxine. Little is known of its chemical properties but thermochemical data for the reaction:

$$H_3B_3O_3(g) + \tfrac{1}{3}B_2O_3(l) \rightarrow H_3B_3O_4(g) + \tfrac{2}{3}B(s)$$

have been tabulated for the range 1020–1303K. The heat of formation of hydroxyboroxine, ΔH_f^0, at 298K $= -1643 \pm 29$ kJ mole^{-1} (-393 ± 7 kcal mole^{-1}).

Trihydroxyboroxine, $H_3B_3O_6$

The monomer HBO_2 is the main boron-containing gaseous species in equilibrium with $B_2O_3(l)$ and $H_2O(g)$ in the temperature range 1061-4151K; the trimer $H_3B_3O_6$ however, believed to be trihydroxyboroxine, **III**, is produced in less than 1% yield.[36]



III

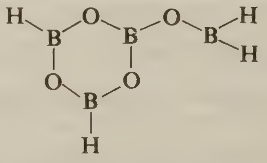
Its heat of formation ΔH_f^0 at 298K has been quoted[19] as -2261 ± 42 kJ mole^{-1} (-541 ± 10 kcal mole^{-1}).

$H_4B_4O_4$

A molecular species with the formula $H_4B_4O_4$ has been identified[37] mass-spectrometrically as a product, in low yields only, of high temperature reactions in the H_2O–B system. For the gas phase reaction:

$$\tfrac{4}{3}H_3B_3O_3 \rightarrow H_4B_4O_4$$

ΔH^0 at 1 200K $= -10{\cdot}5 \pm 8{\cdot}4$ kJ mole^{-1} ($-2{\cdot}5 \pm 2{\cdot}0$ kcal mole^{-1}) and the heat of formation of $H_4B_4O_4(g)$, $\Delta H^0 = -1\,639 \pm 17$ kJ mole^{-1} (-392 ± 4 kcal mole^{-1}) at 298K. This molecule is probably a derivative of boroxine and the structure **IV**, represents a likely configuration:



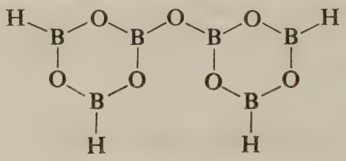
IV

$H_4B_6O_7$

This molecule has also been identified[37] mass-spectrometrically along with $H_4B_4O_4$ in the hydrogen–boron–oxygen system at high temperatures. For the reaction:

$$H_4B_4O_4(g) + B_2O_3(l) \rightarrow H_4B_6O_7(g)$$

ΔH^0 at 1200K $= -3{\cdot}7 \pm 8{\cdot}3$ kJ mole^{-1} ($-0{\cdot}9 \pm 2{\cdot}0$ kcal mole^{-1}), and for $H_4B_6O_7(g)$ $\Delta H^0 = -2888 \pm 21$ kJ mole^{-1} (-691 ± 5 kcal mole^{-1}) also at 1200K. The tentative structure, V, has been proposed for this molecule.



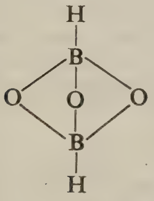
V

$H_2B_2O_3$

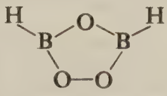
This compound was first observed[38] as an intermediate in the oxidation of pentaborane-9 and was subsequently identified[39] mass-spectrometrically from the same reaction. If oxygen is added slowly to gaseous pentaborane-9 in a borosilicate glass vessel, the reaction is not explosive at ordinary temperatures; the reaction proceeds heterogeneously and products include diborane, hydrogen, solid boric oxide as well as gaseous $H_2B_2O_3$. Alternatively $H_2B_2O_3$ can be prepared by the oxidation of boroxine with molecular oxygen[29, 30], and it has been shown[23] that in the oxidation of pentaborane-9, boroxine is formed initially and further oxidation yields $H_2B_2O_3$. The oxidation of tetraborane and borane carbonyl also yields $H_2B_2O_3$. Isotope distribution experiments indicate that while the precursor to $H_3B_3O_3$ and $H_2B_2O_3$ in the pentaborane–oxygen reaction is probably HBO or H_2BOH, in the tetraborane and borane carbonyl–oxygen reactions the precursor to $H_2B_2O_3$ is probably borane peroxide, H_3BO_2. The reaction of oxygen with trifluorophosphineborane also yields $H_2B_2O_3$.[32]

A convenient laboratory preparation of $H_2B_2O_3$ from diborane has been described.[29] Oxygen is slowly added to diborane held at 20 torr pressure at room temperature in a borosilicate glass bulb, and an electric discharge maintained near the neck of the bulb. Best yields of $H_2B_2O_3$ are obtained with a $B_2H_6{:}O_2$ ratio of 1:1·25.

The infra-red spectrum[39] of gaseous $H_2B_2O_3$ shows a B—H terminal stretching mode and indicates the presence of only one hydrogen per boron atom; it shows no —OH, B—H bridging or B=O groups to be present. The ^{11}B nuclear magnetic resonance spectrum substantiates the presence of a single terminal proton on the boron atoms. Two structures are possible:



VI



VII

Some infra-red evidence favours[39] the D_{3h} trigonal bipyramidal structure **VI**, whilst other infra-red and chemical evidence[23, 29, 40] favours the C_{2v} planar structure **VII**. A molecular orbital treatment shows that the experimental bond lengths are well explained by the π-bond orders.[42] The ultra-violet spectrum shows continuous absorption starting at 2500 Å and extending to shorter wave-lengths.[41]

The thermodynamic stability of $H_2B_2O_3$ and the thermochemistry of its inter-conversion with boroxine have been studied in some detail.[29, 41] Measurements of ΔG^0 for the reaction:

$$H_3B_3O_3(g)+\tfrac{1}{2}O_2(g)\rightarrow H_2B_2O_3(g)+\tfrac{1}{6}B_2H_6(g)+\tfrac{1}{3}B_2O_3(s)$$

lead to an estimate of the heat of formation of $H_2B_2O_3(g)$ at 298K of -838 ± 15 kJ mole^{-1} ($-200{\cdot}4\pm3{\cdot}5$ kcal mole^{-1}).

The compound $H_2B_2O_3$ is unpredictably explosive. It is more stable in the gas phase at room temperature than when stored in a condensed phase at low temperatures. At room temperature, the gas decomposes slowly yielding, amongst the products, diborane and boric oxide. The stability of the gaseous $H_2B_2O_3$ is increased in the presence of added diborane. The known chemical reactions of $H_2B_2O_3$ are confined at present to its inter-conversions with boroxine. It is prepared by oxidation of boroxine and can be converted into boroxine by reaction with diborane.[41] At ordinary temperatures and low pressures, no reaction of $H_2B_2O_3$ with diborane occurs; on application of an electric discharge, however, boroxine is formed. It decomposes photochemically into boric oxide and hydrogen.[41] From mass-spectral patterns obtained from reaction mixtures by adding $^{10}B_2H_6$ to B_2H_6–$H_2B_2O_3$ samples containing the natural $^{10}B/^{11}B$ isotope abundance, and from the observation that higher molecular-weight boranes are formed under the discharge conditions, the reaction is believed to proceed via a BH_3 intermediate[29]:

$$BH_3(g)+H_2B_2O_3(g) \rightarrow H_3B_3O_3(g)+H_2(g)$$

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SECTION A9

ALKALI-METAL BORATES: PHYSICAL AND CHEMICAL PROPERTIES

BY NELSON P. NIES

INTRODUCTION

Gmelin's Handbook[1083] reviews the literature on the lithium borates to 1960, the sodium borates to 1928, and the potassium, rubidium and cæsium borates to 1937. A supplement covering the field to 1973 was published recently.[1083]

Nomenclature, preparation and dehydration were reviewed in 1933.[305] Discussions of aqueous-phase equilibria and other properties appeared in 1956[1107], and in 1964.[1078, 1108] Solubility data are given by Teeple[1116A] and Seidell.[1120A] Anhydrous phase-equilibrium data were given by Levin *et al.* in 1969.[1109] Thermodynamic data were tabulated in 1952[1118] and 1963[1129] and more recently have been calculated for many of the anhydrous lithium, sodium and potassium borates.[1085] Production and technology are reviewed annually.[1112] In the present review, the properties of the various crystalline hydrated and anhydrous borates of each alkali metal are first described. The properties of borate solutions and of molten and glassy borates, including their phase equilibria, are then discussed. Chemical properties of particular borates may be found either in the sections dealing with those borates, or in the general sections on borate solutions, or melts and glasses, as appropriate.

Nomenclature

Some of the names in use for the alkali–metal borates are ambiguous. For example, anhydrous borax, $Na_2B_4O_7$ or $Na_2O,2B_2O_3$ is usually referred to as sodium tetraborate but is sometimes called sodium diborate. The compound $Na_2B_8O_{13}$ or $Na_2O,4B_2O_3$ has also been called sodium tetraborate. The compound $K_2B_4O_7$ is generally named potassium diborate. For $Na_2O,B_2O_3,8H_2O$ (or $NaBO_2,4H_2O$) the names sodium metaborate tetrahydrate and sodium monoborate octahydrate have both been used; and likewise the compound $Na_2O,5B_2O_3,10H_2O$ (or $NaB_5O_8,5H_2O$) has been called both sodium pentaborate pentahydrate and sodium pentaborate decahydrate. It is therefore desirable, if these or similar names are used, to give the formulae as well.

The system of nomenclature currently recommended by the International Union of Pure and Applied Chemistry[357] indicates the number of cations and boron atoms in the simplest stoichiometric unit: $Na_2B_4O_7,10H_2O$, disodium tetraborate decahydrate; $Na_2O,5B_2O_3,10H_2O$ or $NaB_5O_8,5H_2O$, sodium pentaborate pentahydrate; $Na_2B_8O_{13}$, disodium octaborate. Another system, proposed in 1940[370], states the metal oxide to boric oxide molar ratio in parentheses; $Na_2B_4O_7$ would then be sodium (1:2) borate. This system has the advantages of brevity and clarity but has not been frequently used.

Structure

Numerous reviews of the structural chemistry of the borates have been published[101, 160, 163, 169, 230, 435, 485, 819, 832, 1107, 1115, 1119], and principles have been developed to explain and classify their structures.[101, 160, 169, 230, 435, 832] Boron atoms can exist in threefold (triangular-planar) or in fourfold (tetrahedral) coordination to oxygen. If sufficient water is present, the oxygen atoms not shared by two or more boron atoms attach a proton and exist as hydroxyl groups. Polyborate ions are formed from these triangles and tetrahedra by corner-sharing in various ways.

Monomeric and discrete polymeric ions are known, containing usually up to five boron atoms, although the insular groups may polymerize by splitting out water to form ions of much greater size. In ions containing three or more boron atoms, the basic structure is a six-membered ring with alternate boron and oxygen atoms. Two such rings may be fused at a tetrahedral boron atom. The polyions may be linked by shared oxygen atoms to form chains, sheets or three-dimensional networks.[1115] Boric acid groups may exist in isolated form in the presence of complex polyanions, or may polymerize and attach to more complex polyions as side chains.[169] There is usually, but not always[169], a tetrahedral boron atom for each unit of cationic charge.

The structures of borate glasses[342–3, 343A] and of anhydrous borate crystals[343, 1247–8] have been discussed in terms of the 'structon' theory. Advances are being made in the application of magnetic resonance to borate structure determination.[1228, 1252, 829A]

A molecular-orbital calculation on a variety of planar boron–oxygen compounds showed that variations in bond length are reasonably well explained in terms of the π-bond order.[184] Bond lengths suggest that the B–O bonds in boron tetrahedra have a bond number a little smaller than 1; in BO_3 triangles it is a little larger than 1.[1114] Calculations indicated that the size of the π-electron charge on boron varies very little among the various borate structures.[802A]

HYDRATED LITHIUM BORATES

Phase Equilibria in the System Li_2O–B_2O_3–H_2O

Solubility isotherms in the system Li_2O–B_2O_3–H_2O at 10°, 40° and 80°C, and data for the isotherms at 20°, 30° and 60°C have been published.[682] The solid phases found were compounds with $Li_2O:B_2O_3:H_2O$ molar proportions of 1:1:16, 1:1:4, 1:2:3 and 1:5:10. In another study, the dilithium tetraborate hydrate in equilibrium with aqueous solutions was regarded (probably incorrectly) as the 1:2:4 rather than the 1:2:3 compound; the 30°, 58° and 100°C isotherms were also determined.[108, 704] A more recent study of the 100°C isotherm showed the presence of the 2:1:1, 1:1:4, 1:1:1, 1:2:3, 1:2:2, 2:5:7 and 1:5:10 compounds, but there was no evidence for a 1:2:4 compound.[1202A]

Tetralithium Diborate Hydrates

TETRALITHIUM DIBORATE MONOHYDRATE, $Li_4B_2O_5,H_2O$ OR $2Li_2O,B_2O_3,H_2O$

The 2:1:1 compound is in equilibrium with very alkaline solutions at 100°C. Its 100°C isotherm is metastable and its solubility is incongruent. Thermogravimetric analysis showed that it lost its water content at about 200°C.[1202A]

Lithium Metaborate Hydrates

SOLUBILITY DATA

Solubilities in the system $LiBO_2$–H_2O are presented in Table I. In connection with the transition point at 36·9°C, it should be noted that thermal analysis showed the transition at 40°C.[108] The solubility values at temperatures above 37°C given in Mellor, V, p. 65, are much higher than the values in Table I because they refer to solutions saturated with $LiBO_2,8H_2O$ and supersaturated with respect to $LiBO_2,2H_2O$. Other measurements on this metastable curve (wt-% $LiBO_2$) are: 40°, 9·40; 42°, 34·10; 44·8°, 14·7; 46°, 29·97; and 47·1°, 25·67.[682]

Table I.—Solubility of Lithium Metaborate in Water

Temperature, °C	Solubility, wt-% of $LiBO_2$	Solid phase	Reference
−0·515	0·75	$LiBO_2$, $8H_2O$ and ice (cryohydric point)	562
0	0·88	$LiBO_2$, $8H_2O$	682
10	1·42		682
18	2·203		559
20	2·51		682
23·5	3·12		108
25	3·344		559
30	4·63		682
30·8	5·00		108
34	5·97		682
34·5	6·16		108
36·9	7·2	Transition point, $LiBO_2,8H_2O$ to $LiBO_2,2H_2O$	682
37	7·26	$LiBO_2,2H_2O$	682
38	7·33		682
39	7·34		682
40	7·40		682
50	7·84		682
56	8·29		108
60	8·43		682
61	8·66		108
65	8·90		108
70	9·48		682
78	9·80		108
80	10·58		682
80	9·75		108
100	9·70		108
101·2	13·4		682
125	9·90		108
150	8·75		108
180	8·30	$LiBO_2,\frac{1}{2}H_2O$	108
200	7·90		108
225	3·20		108
245	2·85	$LiBO_2$	108
275	2·60		108

LITHIUM METABORATE OCTAHYDRATE, $LiBO_2,8H_2O$ OR $Li_2O,B_2O_3,16H_2O$

The 1:1:16 compound, of which the crystal structure is trigonal[559], is stable in contact with its solution below 36·9°C.[682] A published *X*-ray pattern, said to be that of the 1:1:16 compound[107], appears to be largely that of the 1:1:4 compound[724, 1202A] instead. The structure contains the $B(OH)_4^-$ and $Li(OH_2)_4^+$ ions.[933A] The infra-red absorption spectrum[315] is similar to that of $NaBO_2,2H_2O$, which has a tetrahedral borate group. The 1:1:16 compound can be obtained readily in pure state, and it has been suggested as a titrimetric standard.[559] It has been recommended as a component of a shielding material for neutrons and γ-rays[989] and has some advantages as a component of a scintillator for detecting slow neutrons.[876]

When the octahydrate is dehydrated at 16°C over concentrated sulphuric acid, six of the eight molecules of water are lost in about 45 days, but only 0·5 molecule more is lost in the next 300 days.[559] This behaviour accords with the presence of the $B(OH)_4^-$ ion. Thermogravimetric analysis with a heating rate of 30° per hour[107–8] also shows a rapid loss of six of the eight molecules of water, below 70°C. Between 70° and about 140°C, the water content remains constant at the $LiBO_2,2H_2O$ composition. The last two molecules are lost between 140° and 280°C.

LITHIUM METABORATE DIHYDRATE, $LiBO_2,2H_2O$ OR $Li_2O,B_2O_3,4H_2O$

The 1:1:4 compound is orthorhombic and has a calculated density of 1·825.[724] It did not appear in early solubility studies (Mellor, V, p. 65) but was crystallized first by Reburn and Gale[682], who determined its solubility (*v. supra*) and found it to be the stable phase above 36·9°C in contact with its solution.

The *X*-ray diffraction pattern has been published[724]; another published pattern[107] appears to be incorrectly identified since it corresponds closely with that of the corresponding sodium compound. The structure of $LiBO_2,2H_2O$ consists of isolated $B(OH)_4$ tetrahedra, linked to LiO_4 tetrahedra by common edges and hydrogen bonds.[334, 338, 469] Unit-cell data are reported.[634] The infra-red spectrum has been studied.[391]

Thermal analysis studies under pressure indicate that the 1:1:4 compound decomposes at 150°C in contact with its saturated solution to give the 1:1:1 compound.[107–8]

The 1:1:4 compound is stable in air.[634] When heated, it begins to lose water below 200°C, and becomes amorphous at 200°. Partial crystallization takes place during heating to 250°C, and well-crystallized $LiBO_2$ is present at 450°C.[724] Thermogravimetric studies have been made.[1255]

LITHIUM METABORATE HEMIHYDRATE, $LiBO_2,\frac{1}{2}H_2O$ OR Li_2O,B_2O_3,H_2O

According to solubility and thermal analysis studies under pressure[107–8] the 1:1:1 compound is in equilibrium with its solutions under pressure from 150° to 250°C, where it decomposes to give the anhydrous salt. Its solubility at these temperatures (*v. supra*) decreases with increased temperature.[108] At 100°C its solubility is incongruent. Its 100°C isotherm is partly stable and partly metastable.[1202A] The *X*-ray diffraction pattern has been published.[107]

Dilithium Tetraborate Hydrates

DILITHIUM TETRABORATE TRIHYDRATE, $Li_2B_4O_7,3H_2O$ OR $Li_2O,2B_2O_3,3H_2O$

Most investigators of the lithium borates agree on the basis of analysis of the wet residue or the dried solid[280, 493, 682, 967, 1202A], that the stable phase in equilibrium with dilithium tetraborate solution between the freezing and boiling points is the 1:2:3 compound of density 1·88.[280] A phase diagram of the $Li_2B_4O_7$–H_2O system from −3° to 387°C has recently been drawn from solubility and heating-curve studies under pressure.[1203] These studies have shown that the 1:2:3 compound is the stable phase in contact with its solution from −3° to 150°C, where the 1:2:2 compound becomes stable.[1203] Previously the heat effect at 150°C had been thought to be the transition point from the 1:2:4 to the 1:2:3 compound.[107–8] When gradually heated under pressure, the 1:2:3 compound tends to persist in the temperature region where it is metastable, i.e. above 150°C. In this case it changes to the 1:2:1 compound at 194°C, in contact with its saturated solution (containing about 7·5% of $Li_2B_4O_7$).

Evidence[104, 107–8, 702] that this compound is the tetrahydrate rather than the trihydrate is of doubtful value, as the *X*-ray diffraction pattern[107] of the alleged tetrahydrate is identical with that of the trihydrate dried at 100°C.[648, 1154] Another pattern of a 'trihydrate', which was said to be always accompanied by the pattern of the anhydrous salt, was reported[107] but has not been confirmed in other studies.[648] A pattern (card (1-112)) in the A.S.T.M. Powder Diffraction File[1114A], said to be that of a pentahydrate, apparently refers to the trihydrate.[648] The trihydrate can, under appropriate conditions, absorb a considerable quantity of water. Compositions containing up to 40% of water (>6 molecules) have been prepared[648], and they give the same *X*-ray diffraction pattern as the trihydrate.[648]

The solubility of the trihydrate has been reported in two different papers[682, 108], but in the second of these the solid phase was regarded as $Li_2B_4O_7,4H_2O$; data are given in Table II. The freezing point of a solution saturated with the 1:2:3 compound is −3°C.[1203]

The trihydrate crystallizes with difficulty from a supersaturated solution prepared by adding boric acid to lithium hydroxide solution. When allowed to stand, solutions containing 20–25% of $Li_2B_4O_7$ deposit a gelatinous $Li_2B_4O_7$ hydrate having

Table II.—Solubility of Dilithium Tetraborate in Water

Temperature, °C	0	10	20	25	28	30	34·5	40	45·9	56·1	60	61	65	76·5	80	100
Solubility, wt-% of $Li_2B_4O_7$, ref. (682)	2·20	2·55	2·81			3.01		3·26			3·76				4·35	5·17
Ditto, ref. (108)	2·50		2·75	2·90	2·95	3·05	3·10	3·21	3·41	3·67		3·80	3·96	4·30	4·40	5·50

an indefinite water content.[682] When such solutions are boiled for one to four hours, crystalline trihydrate is formed.[682] Slow cooling is said to avoid the formation of other hydrates.[967] An aqueous solution of lithium carbonate and boric acid also forms fine white crystals of $Li_2B_4O_7,3H_2O$ over a period of several weeks.[280] A thermogravimetric curve of wet crystals from solubility determinations showed that at 50° [1203], 60° or 70°C[107] the water content decreased to three molecules. This composition was maintained up to 180°.[1203] Above 180°, more water was lost and formation of the anhydrous salt was complete at about 320°.[107] There was no indication of a tetrahydrate stage in the thermogravimetric curves. Some trihydrate crystals persisted when a sample was dehydrated to the 1:2:2 composition at 260°C, as indicated by the diffraction pattern.[648] In another study all the water of the trihydrate was lost between 200° and 220°C.[280] In a sealed tube at 200° the wet 1:2:3 compound readily changed to the 1:2:2 compound.[1202A]

A DTA curve of $Li_2O,2B_2O_3,3H_2O$ showed endothermic effects at 290°C (dehydration) and at 890° (fusion).[493]

DILITHIUM TETRABORATE DIHYDRATE, $Li_2B_4O_7,2H_2O$ OR $Li_2O,2B_2O_3,2H_2O$

The 1:2:2 compound, easily prepared by heating the wet 1:2:3 compound in a sealed tube at 200°C, is metastable and incongruent at 100°C; its 100°C isotherm has been determined.[1202A] According to solubility and heating-curve experiments under pressure, it is in equilibrium with its solution from 150° to 272°C. At 272°C it decomposes to give the 1:2:1 compound and a solution containing 7·52% of $Li_2B_4O_7$.[1203] This thermal effect was previously thought[108] to be due to a 1:2:3-anhydride transition. Thermogravimetric analysis of the 1:2:2 compound gives two plateaux, one at 50–220°C and one, presumably corresponding to the 1:2:1 compound, at 250–350°C.[1203]

DILITHIUM TETRABORATE MONOHYDRATE, $Li_2B_4O_7,H_2O$ OR $Li_2O,2B_2O_3,H_2O$

The 1:2:1 compound, formed from the 1:2:3 compound above 194°C or from the 1:2:2 compound above 272°C in heating curve experiments under pressure, is the stable phase in equilibrium with its solution from 272° to 387°C, where it decomposes to form the anhydrous salt in contact with its saturated solution containing about 10% of $Li_2B_4O_7$. Its *X*-ray diffraction pattern can be obtained from a sample previously heated for a long period in a sealed tube.[1203]

Tetralithium Decaborate Hydrates

TETRALITHIUM DECABORATE HEPTAHYDRATE, $Li_4B_{10}O_{17},7H_2O$ OR $2Li_2O,5B_2O_3,7H_2O$

The 2:5:7 compound is stable in contact with solutions at 100°C, but its solubility is incongruent. Its 100°C isotherm has been published.[1202A] Its thermogravimetric curve shows that water loss begins at 120°C and stops between 160° and 220°C at the 2:5:5 composition. Further heating leads to the anhydrous salt. The *X*-ray diffraction pattern of the 2:5:7 compound could be obtained after drying at 100°C. The pattern of the 2:5:5 compound could not be obtained.[1202A]

Lithium Pentaborate Hydrates

LITHIUM PENTABORATE PENTAHYDRATE, $LiB_5O_8,5H_2O$ OR $Li_2O,5B_2O_3,10H_2O$

The 1:5:10 compound has an incongruent solubility below 37·5°C [108], or 40·5°C.[682] Solubility values are listed in Table III. Published values determined

Table III.—Solubility of Lithium Pentaborate in Water

Temperature, °C	37·5	45	45·9	50	60	65	70	80	100
Solubility, wt-% of LiB_5O_8, ref. (682)		19·27		20·88	24·34		27·98	31·79	
Ditto, ref. (108)	17·90		20·60			27·05		32·25	41·20

under pressure at 150–300°C [108] do not agree with a diagram published later.[1201A] The *X*-ray diffraction pattern of the 1:5:10 compound has been published.[107,724] A study of heating curves and of solubility under pressure indicated that the 1:5:10 compound changed to the 1:5:2 compound at 140°C in contact with a solution containing 52 wt-% of LiB_5O_8.[1201A] The 1:5:2 compound was stable under pressure up to 265°, where it decomposed to give the 1:5:1 compound in contact with a solution containing 72·5 wt-% of LiB_5O_8.[1201A] A plateau at 462°C under pressure was ascribed to the decomposition of the 1:5:1 compound to form the anhydrous salt in contact with a solution containing an estimated 84 wt-% of LiB_5O_8. Thermogravimetric curves show a loss of about 7·5 molecules of water between 110° and 200°C and a loss of nine molecules of water at 300°C. There were inflections at the 1:5:2 and 1:5:1 compositions.[1201A] A sample preheated in a sealed tube showed more definite plateaux at these compositions. Loss of water was complete at about 450°C.[107–8]

LITHIUM PENTABORATE MONOHYDRATE AND HEMIHYDRATE, LiB_5O_8,H_2O AND $0{\cdot}5H_2O$, OR $Li_2O,5B_2O_3,2H_2O$ AND H_2O

Thermogravimetric curves of the 1:5:10 compound suggest the existence of a 1:5:2 compound. This has been isolated and its solubility determined between 140° and 264°C.[1201A] The existence of a 1:5:1 compound was also indicated by the thermogravimetric curve of the 1:5:10 compound.[1201A] The *X*-ray diffraction pattern of a product dried to a 5% water content (1·1 molecules) has been published.[107] It was thought at first to be the pattern of the 1:5:1 compound[107], but was indicated by later work to be that of the 1:5:2 compound.[1201A]

ANHYDROUS LITHIUM BORATES

Phase Equilibria in the System Li_2O–B_2O_3

Phase equilibrium studies by thermal analysis[703] and by the quenching and differential thermal analysis[108A] methods have indicated that crystalline compounds exist with the following $Li_2O:B_2O_3$ molecular ratios: 3:1 (α- and β-forms), 3:2, 2:1 (α- and β-forms)[725], 1:1, 1:2, 2:5, 1:3 and probably 1:4.[108A,724] There are eutectics at 52 wt-% B_2O_3, m.p. 650 ± 15°C[724–5] (or 53 wt-% B_2O_3, m.p. 665° [108A]), and at 72 wt-% B_2O_3, m.p. 832 ± 2°C[724–5] (or 74 wt-% B_2O_3[108A]).

The heats of solution of devitrified compositions in the Li_2O–B_2O_3 system reached a minimum at 25 mol-% Li_2O.[750,783]

Crystalline Anhydrous Lithium Borates

TRILITHIUM MONOBORATE OR LITHIUM ORTHOBORATE, Li_3BO_3 OR $3Li_2O,B_2O_3$

The 3:1 compound exists in high- and low-temperature modifications, with a transition point at 690°C[483] or 700°C.[108A] The low-temperature form, monoclinic, *d* (calc.) 2·161 g cm^{-3}, referred to both as the α-form[798A] and as the β-form[108A], crystallizes from its melt in small needles[703,798A] or from a $5Li_2O,B_2O_3$ melt in larger crystals 0·1 mm in diameter.[798A] Its *X*-ray diffraction pattern[483] and its infrared absorption spectrum[744A] have been reported. It has an unusual structure consisting of isolated planar BO_3 groups, distorted LiO_4 tetrahedra, large holes and $(Li–O)_3$ rings.[798A] It is relatively unreactive with atmospheric moisture.[798A] It forms a continuous series of solid solutions with lithium carbonate.[483]

The high-temperature form, referred to both as the β-form[798A] and as the α-form[108A], was not observed in some phase-equilibrium studies in which the low-temperature form was regarded as melting incongruently at 695°C[703] or at 715 ± 15°C.[725] In another study, however, an *X*-ray diffraction pattern appeared at temperatures above 690°C which was different from the patterns of possible decomposition products.[483] This high-temperature form is probably monoclinic. Its unit cell data have been reported.[798A] The structure did not persist on cooling, even with quenching.[108A, 483] A phase diagram based on differential thermal analysis shows either a decomposition of the high-temperature form at 730°C to give, as stable products, lithium oxide and a liquid containing 48 wt-% of B_2O_3, or a metastable fusion at 760°C.[108A] Complete melting of the 3:1 compound occurs at 815°C.[483]

Two other low-temperature forms have been observed. At temperatures between 300° and 350°C an unidentified phase was obtained. Heating for 4 h at 400°C gave the ordinary low-temperature form plus a new phase, the *X*-ray pattern of which could be indexed in the cubic system[798A] with $a = 6{\cdot}146$. This phase disappeared after heating for 24 h at 400°C. The molten 3:1 compound, made by melting together lithium carbonate and a lithium borate, can be made carbonate-free by passing a current of air, free from carbon dioxide, over it at 850°C for 10 h.[483]

TETRALITHIUM DIBORATE, $Li_4B_2O_5$ OR $2Li_2O,B_2O_3$

This 2:1 compound exists in two polymorphic forms. The α-form is stable from 600 ± 6° to 618 ± 6°C[725], and the β-form from 618 ± 6° to 650 ± 15°C.[725] Below 600 ± 6°C the α-form dissociates to form the 3:2 and 3:1 lithium borates. When heated to 650 ± 15°C the β-form may also dissociate to form the 3:2 and 3:1 compounds, although the data can also be interpreted by incongruent melting.[725] Both forms of the 2:1 compound can be quenched to room temperature. Their *X*-ray diffraction patterns have been tabulated.[725] In another study by differential thermal analysis, only one form (orthorhombic) was observed, decomposing at 645°C to give the 3:1 (low-temperature form) and β-3:2 compounds.[108A]

HEXALITHIUM TETRABORATE, $Li_6B_4O_9$ OR $3Li_2O,2B_2O_3$

Two forms of this 3:2 compound have been reported. The β-form crystallizes at about 600°C and can be obtained at room temperature by quenching in liquid nitrogen.[108A] The α-form crystallizes above 650°C.[108A] It forms thick crystals 2–3 mm in size[108, 703] and melts incongruently at 700° ± 6°C[708A, 725] or at 685°C[108] to give the β-1:1 compound and a liquid containing 37·5 mol-% (57·3 wt-%) of B_2O_3.[108A] Its *X*-ray diffraction pattern has been tabulated.[725]

LITHIUM METABORATE, $LiBO_2$ OR Li_2O,B_2O_3

Like metaboric acid, this 1:1 compound exists in forms having boron atoms in 3-, 3- and 4-, and 4- coordination.[149] The α-form, monoclinic, congruent m.p. 849°C[108A, 724], 840°C[108], or 833–836°C[649], *d* (calc) 2·223[932]; (obs.) 2·18[932] or 2·14[335] g cm^{-3}, crystallizes from the melt in flat needles. Photomicrographs of the crystals have been published.[724] The *X*-ray diffraction pattern has been tabulated.[107, 724] The structure consists of endless chains of BO_3 triangles as in CaB_2O_4[315]; Li–O bonds between chains give the crystals a fibrous character.[335, 932] It is thus different from the structures of the corresponding sodium and potassium compounds, which contain insular $[B_3O_6]^{3-}$ groups. The structure has been discussed in terms of the 'structon' theory.[1247] The infra-red spectrum[899] is entirely different from the spectra of the sodium and potassium metaborates.

The thermal expansion of lithium metaborate is non-linear above about 200°C. An increase in temperature from 200° to 600°C increases the expansion coefficient. A decrease in temperature from 600° to 300°C causes a contraction, but a decrease from 300° to room temperature causes an expansion.[724]

A tetragonal 'γ'-form, changing to the β-form at 580°C, and a 'β'-form with a metastable fusion at 822°C have been reported from differential thermal analysis studies.[108A]

Another 'γ'-form, $LiBO_2$,0·05 to 0·35H_2O, crystallizes from the amorphous product of the dehydration of the 2-hydrate at 200°C. A structure comparable with that of crystalline boric oxide or γ-metaboric acid is thought probable.[482] It is stable up to about 350°C, at which it is converted into another 'β'-form, $LiBO_2, \leq 0{\cdot}02H_2O$, which is metastable.[482] This β-form has the low (α)-cristobalite structure[482], with all boron atoms tetrahedrally coordinated by oxygen, as is shown by the similarity of its infra-red spectrum to that of compounds containing tetrahedral boron.[315] By long heating at temperatures as low as 350°C, or by heating to 580°C, it is converted into the stable α-form.[482] *X*-ray diffraction patterns have been tabulated for two forms of lithium metaborate obtained by slow cooling of the melt and by dehydration of $LiBO_2$,8H_2O at 500°C.[107] These patterns differ from each other and from the pattern of the α-form.

At 15 kilobars and 230°C the α-form changes to another 'β'-form having both 3- and 4-coordinated boron atoms, as shown by infra-red spectra.[149] The *X*-ray pattern of this β-form has been tabulated.[149] This form changed back to the α-form when heated for 3 h at 400°C in air.[149] At 18 kilobars and 370°C[149], or 35 kilobars and 850°C[527], a tetragonal α-modification (*d* (calc.) 2·883 g cm^{-3}) was formed.

Single crystals of another 'γ'-form, stable at high pressure and temperature, have been grown at 15 kilobars and 950°C in a flux of lithium chloride.[528] Its *X*-ray diffraction pattern has been indexed and tabulated.[527] Its infra-red absorption spectrum indicates that all its boron atoms are in fourfold coordination.[149] Its structure consists of a three-dimensional array of LiO_4 and BO_4 tetrahedra having only vertices in common. The tetrahedra are arranged like those in sphalerite.[527–8] The structure has been discussed in terms of the 'structon' theory.[1247]

The thermoluminescent properties of lithium metaborate activated with manganese have been investigated, and this material has been used as a dosimeter for β-rays.[1157] Lithium metaborate also has some desirable properties as a constituent of a scintillator for the detection of slow neutrons, but it is brittle when pressed and its transparency is poor.[876]

Heat capacity, entropy, free-energy function, enthalpy, and heat and free energy of formation have been calculated and tabulated for crystalline $LiBO_2$ from 0 to 2500 K, for crystalline $Li_2B_2O_4$ from 0 to 2000 K, for liquid $LiBO_2$ from 298 to 4000 K, for liquid $Li_2B_2O_4$ from 298 to 5000 K, and for gaseous $LiBO_2$ from 0 to 6000 K.[1085] Values of heat capacity, entropy, and $(H-H_0)/T$ for crystalline $LiBO_2$ have also been tabulated from 15 to 298 K.[800A] A heat-capacity study at 55–300°C indicated a polymeric structure.[855]

Cryoscopic studies on sodium, lithium and barium chlorides, lithium oxide, and boric oxide in molten lithium metaborate have indicated the cryoscopic constant to be 15 and the molar heat of fusion to be 8·3 kcal $mole^{-1}$.[939] From the freezing-point diagram of the $LiBO_2$–LiF system, the heat of fusion of the metaborate was evaluated as 7·4 kcal $mole^{-1}$.[649]

Lithium metaborate, heated with magnesium oxide, forms Li_2O,2MgO,B_2O_3 and Li_2O,MgO,B_2O_3, which have incongruent melting points.[486] Heating of the metaborate (in excess) with zinc oxide[480], manganese oxide[480] or cobaltous oxide[480–1], affords the compound $LiZnBO_3$, $LiMnBO_3$ or $LiCoBO_3$; these compounds melt incongruently with formation of zinc, manganous or cobaltous oxide. Infra-red spectra of $LiMgBO_3$, $LiMnBO_3$, $LiCoBO_3$ and $LiZnBO_3$ indicate the presence of the BO_3^{3-} ion, the boron being trivalent.[480] *X*-Ray patterns have been reported.[480] The infra-red absorption spectrum of crystalline Li_2O,B_2O_3,2GeO_2 has been studied.[1181] Lithium metaborate is an effective flux in silicate analysis.[352A] Applied to an alumina tube as a slurry in ethanol, and heated at 850°C, lithium metaborate made the tube vacuum-tight even at elevated temperatures.[1005]

DILITHIUM TETRABORATE, $Li_2B_4O_7$ OR Li_2O,2B_2O_3

This 1:2 compound, congruent m.p. 917°C, crystallizes from the melt in long needles[108, 703] or rounded to hexagonal crystals.[724] Its structure[452, 458] consists of two interlocking three-dimensional networks made up of twisted double-ring groups. These borate groups have two boron atoms with trigonal and two with tetrahedral coordination and are similar to the borate ion found in borax (p. 362). A linear structure has been indicated by heat-capacity studies.[550A] The structure has been discussed in terms of the 'structon' theory.[1247] The crystals are biaxial and negative, and have a high birefringence. The indices of refraction have been reported and photomicrographs of the crystals have been published.[724]

The 1:2 compound, when previously melted with manganous chloride and crystallized by cooling in argon, has good thermoluminescent properties.[1042] A product with reproducible thermoluminescent properties can also be made by fusing lithium carbonate with boric acid and manganous chloride at 950°C.[1146] Other studies have been made of the thermoluminescent properties of $Li_2B_4O_7$ activated by manganese.[12A, 724, 821, 1157–8] It was fluorescent under cathode excitation but not under ultra-violet light.[724] Its n.m.r. spectrum has been compared with computer-simulated spectra.[60] The linear coefficient of expansion is $13{\cdot}8 \times 10^{-6}$ per °C.[724]

The bulk density of granular $Li_2B_4O_7$ is 50–60 lb ft^{-3} if it is prepared by slowly heating a mixture of $LiOH,H_2O$ and boric acid, in the presence of recycled product, to a temperature of 550–650°C. In contrast, the product made by calcining material deposited from aqueous solution is a fine powder which has a bulk density of only 15–25 lb ft^{-3}.[966]

From experimental heats of solution in nitric acid and high-temperature calorimetric measurements, the enthalpy and entropy have been determined and tabulated for dilithium tetraborate crystals from 100° to 917°C and for the molten compound from 100° to 1100°C.[780, 783] In another study, the heat capacity of the crystals was measured at 70–300 K.[550A] The heat capacity, entropy, free-energy function, enthalpy and heat and free energy of formation have been calculated and extrapolated for crystalline $Li_2B_4O_7$ from 298 to 2000 K, and for molten $Li_2B_4O_7$ from 298 to 3000 K.[1085] The heat of fusion at the melting point is 170 g cal g^{-1} and the heat of devitrification at 25°C is $-65{\cdot}5$ g cal g^{-1}.[780]

TETRALITHIUM DECABORATE, $Li_4B_{10}O_{17}$ OR $2Li_2O,5B_2O_3$

This 2:5 compound, m.p. (incongruent) 856°C, forms very small crystals. It dissociates at temperatures below 696°C to form $Li_2O,2B_2O_3$ and $Li_2O,3B_2O_3$.[724] Its *X*-ray diffraction pattern has been published.[724]

LITHIUM TRIBORATE, LiB_3O_5 OR $Li_2O,3B_2O_3$

The 1:3 compound, m.p. (incongruent) 834°C[724] or 840°C[703] dissociates at temperatures below 595°C to form the 1:2 and 1:4 compounds.[724] The *X*-ray diffraction pattern[724] and the infra-red spectrum[899] have been reported. From measurements of heat of solution[750] and high-temperature enthalpy[783], the heat capacity, entropy, free-energy function, enthalpy, heat of formation and free energy of formation have been tabulated for crystalline $Li_2O,3B_2O_3$ from 298 to 2000 K[1085] and for molten $Li_2O,3B_2O_3$ from 298 to 5000 K.[1085]

DILITHIUM OCTABORATE, $Li_2B_8O_{13}$ OR $Li_2O,4B_2O_3$

This 1:4 compound apparently exists in two crystalline forms.[107–8] The stable form, prepared by heating at 600°C for 12–14 h[107], has been found by the heating-curve method to decompose at 790°C forming the 1:3 compound and a liquid containing 89 wt-% of B_2O_3. Its *X*-ray diffraction pattern has been reported.[107] This form did not appear in another investigation.[724]

The metastable form melts incongruently at 635 ± 10°C, according to quenching experiments[724], but at 730°C according to a heating-curve investigation.[107] The difference may be due to the extremely low rate at which equilibrium is reached in this system at high boric oxide contents and temperatures near or below 600°C. The *X*-ray diffraction pattern of the metastable form has been published.[724]

The thermoluminescence properties of $Li_2O,4B_2O_3$ activated with manganese

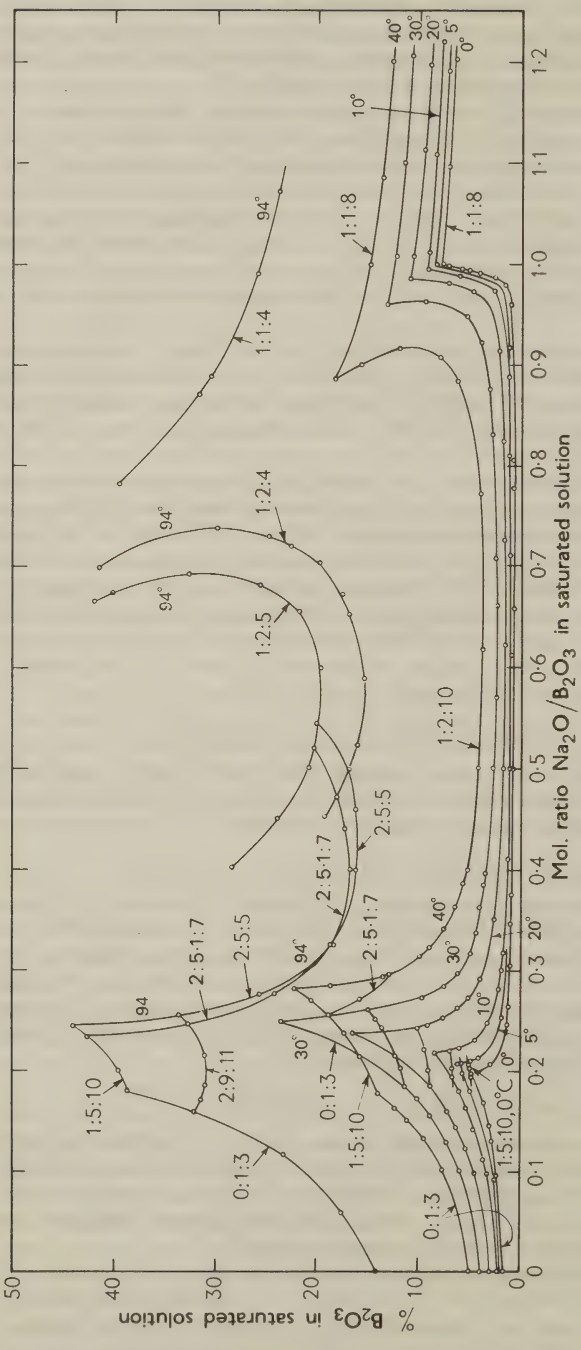

FIG. 1a.—Solubility isotherms in the system Na_2O–B_2O_3–H_2O at 0°, 5°, 10°, 20°, 30°, 40°, 50° and 94°C[619, 619A]

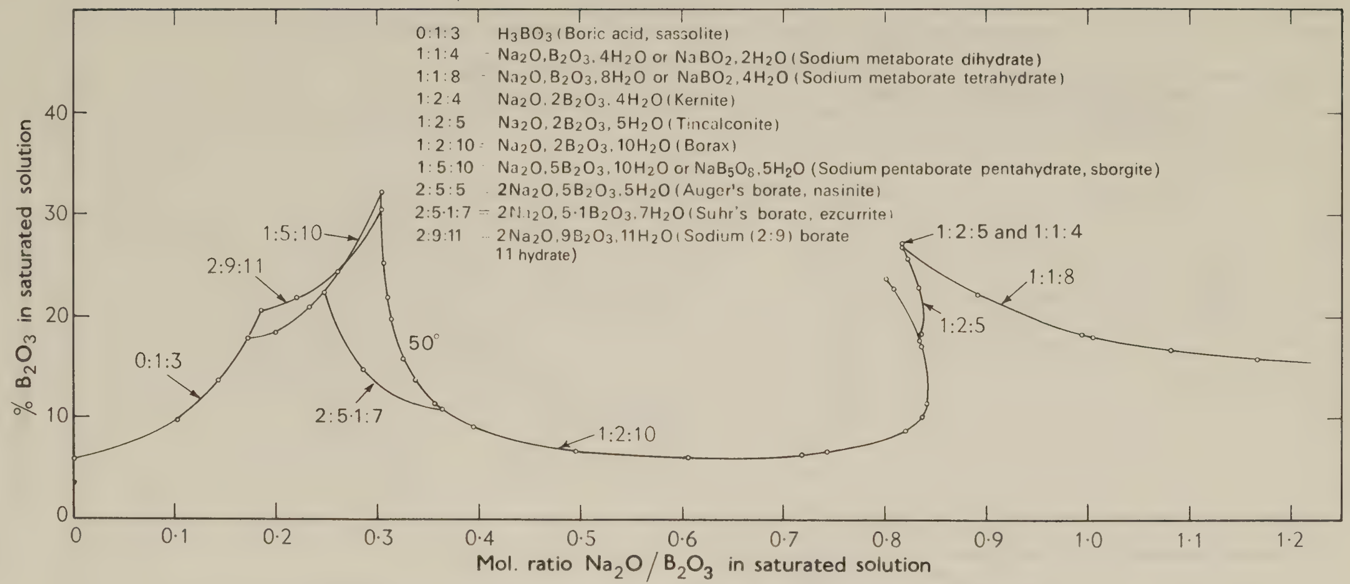

FIG. 1b.—Solubility isotherm in the system Na_2O–B_2O_3–H_2O at 50°C[619, 619A]

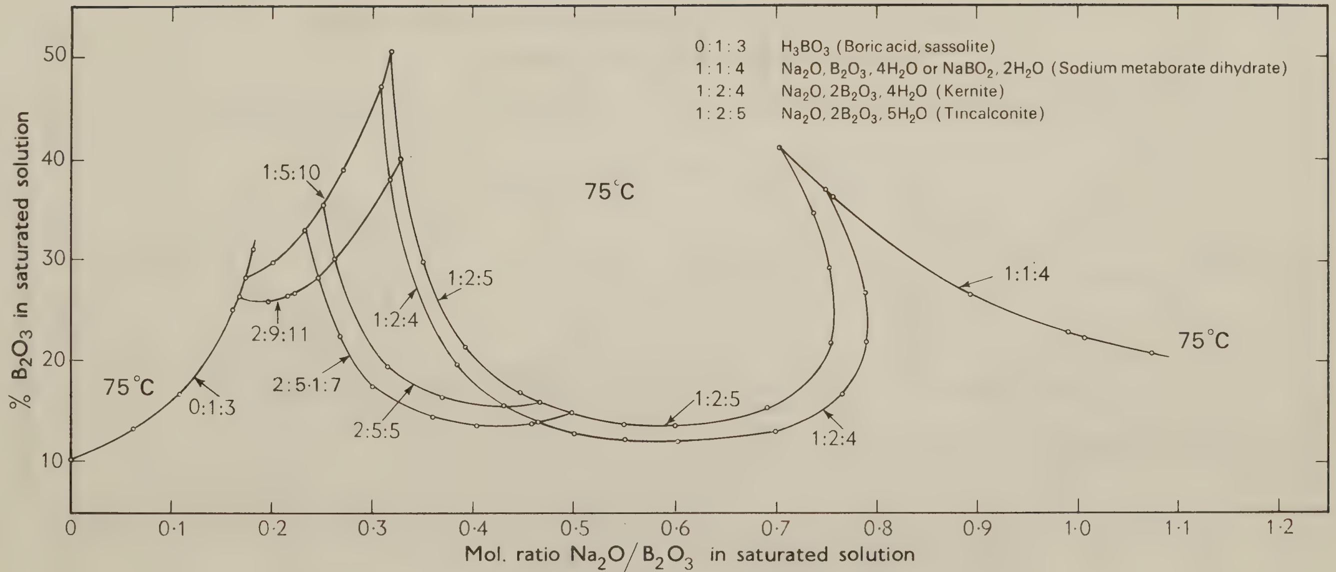

FIG. 2a.—Solubility isotherms in the system Na_2O–B_2O_3–H_2O at 75°C[619, 619A]

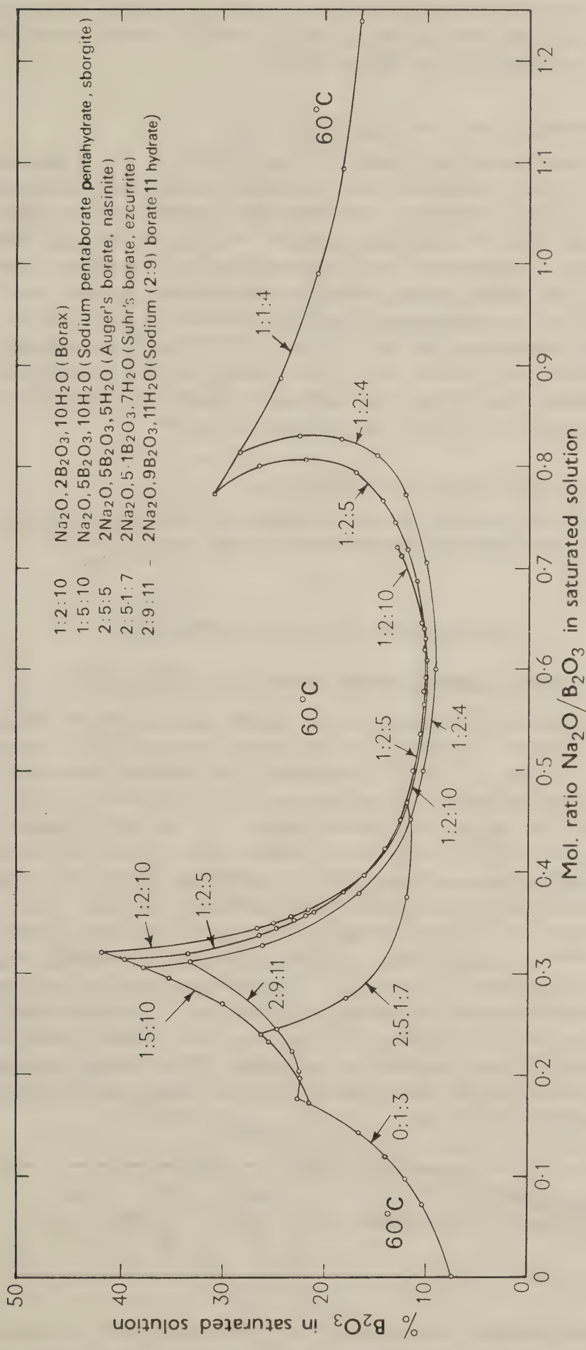

FIG. 2b.—Solubility isotherms in the system Na_2O–B_2O_3–H_2O at 60°C[619, 619A]

have been investigated.[1157] $Li_2O,4B_2O_3$ has a high absorption capacity for neutrons and gamma rays.[989]

From heat of solution[750] and high-temperature enthalpy measurements[783] the heat capacity, entropy, free-energy function, enthalpy, heat of formation and free energy of formation have been tabulated for $Li_2O,4B_2O_3$ crystals from 298 to 2000 K and for molten $Li_2O,4B_2O_3$ from 298 to 5000 K.[1085]

LITHIUM PENTABORATE, LiB_5O_8 OR $Li_2O,5B_2O_3$

This 1:5 compound does not crystallize from the melt, but it has been thought to form when $Li_2O,5B_2O_3,10H_2O$ is dehydrated at 400°C and reheated for 3 days at 300–350°C.[108] *X*-Ray diffraction indicated the presence of the monohydrate in small amounts, but did not show any pattern attributable to $Li_2O,5B_2O_3$. If this phase was formed, it apparently did not crystallize well enough to give an *X*-ray powder pattern. The heating curve showed a pronounced plateau at 475°C, which was considered to be the incongruent melting point of $Li_2O,5B_2O_3$ to give $Li_2O,4B_2O_3$ and a liquid containing 99 wt-% of B_2O_3.[108] If the heat treatment of the dehydrated decahydrate was above 400°C, the plateau in the heating curve did not occur and $Li_2O,4B_2O_3$ was formed. An infra-red absorption spectrum of a material regarded as crystalline $Li_2O,5B_2O_3$ has been published.[899]

LITHIUM ENNEABORATE, LiB_9O_{14} OR $Li_2O,9B_2O_3$

The heat content and entropy of a 1:9 composition, before and after devitrifying at 550°C for 48 h, has been determined between 100° and 1100°C.[783]

HYDRATED SODIUM BORATES

Phase Equilibria in the System $Na_2O–B_2O_3–H_2O$

A study of the solubility isotherms of the stable and metastable sodium borates at temperatures from 0° to 94°C, in the range of $Na_2O:B_2O_3$ molecular ratio 0 to 1·2 (Figs. 1 and 2)[619, 619A], extended the earlier investigations[93, 730–2] (Mellor, V, p. 67) and corrected some inaccuracies. Another study (Fig. 3)[421A, 471A] included isotherms for the whole system, from −30° to 100°C, gave polythermic diagrams showing the stability regions of twelve sodium borate hydrates which are stable in contact with solutions up to 100°C, and listed the invariant points. These diagrams do not show the area above 87°C, between the 2:5:7 and 1:2:4 compounds, in which the stable phase is Auger's sodium borate, $2Na_2O,5B_2O_3,5H_2O$.[619, 619A] A polythermic diagram showing the stability regions of the sodium metaborates and the 2:1:1 and 2:1:5 compounds has also been published.[421] A patent[958] gives information on the solubility of the 1:1:4 compound in the presence of sodium hydroxide. Further studies have been made of the 25°[863A] and 100°[106] isotherms. The compositions of solutions in the ternary system saturated with both Auger's borate and disodium tetraborate monohydrate ($Na_2B_4O_7,H_2O$) have been reported[1058] as follows:

Temperature, °C	150	175	195
Moles Na_2O per mole B_2O_3	0·56	0·502	0·46
% H_2O	61	49	38

The Auger's borate solubility isotherm at 150°C has been partly determined in two studies, with different results.[570, 1058] An investigation of the ice fields in this system showed that the ternary eutectic, containing Na_2O 2·37, B_2O_3 1·92 mole-% freezes at −6·8°.[468] Earlier solubility data have been summarized.[1082, 1116A, 1120A]

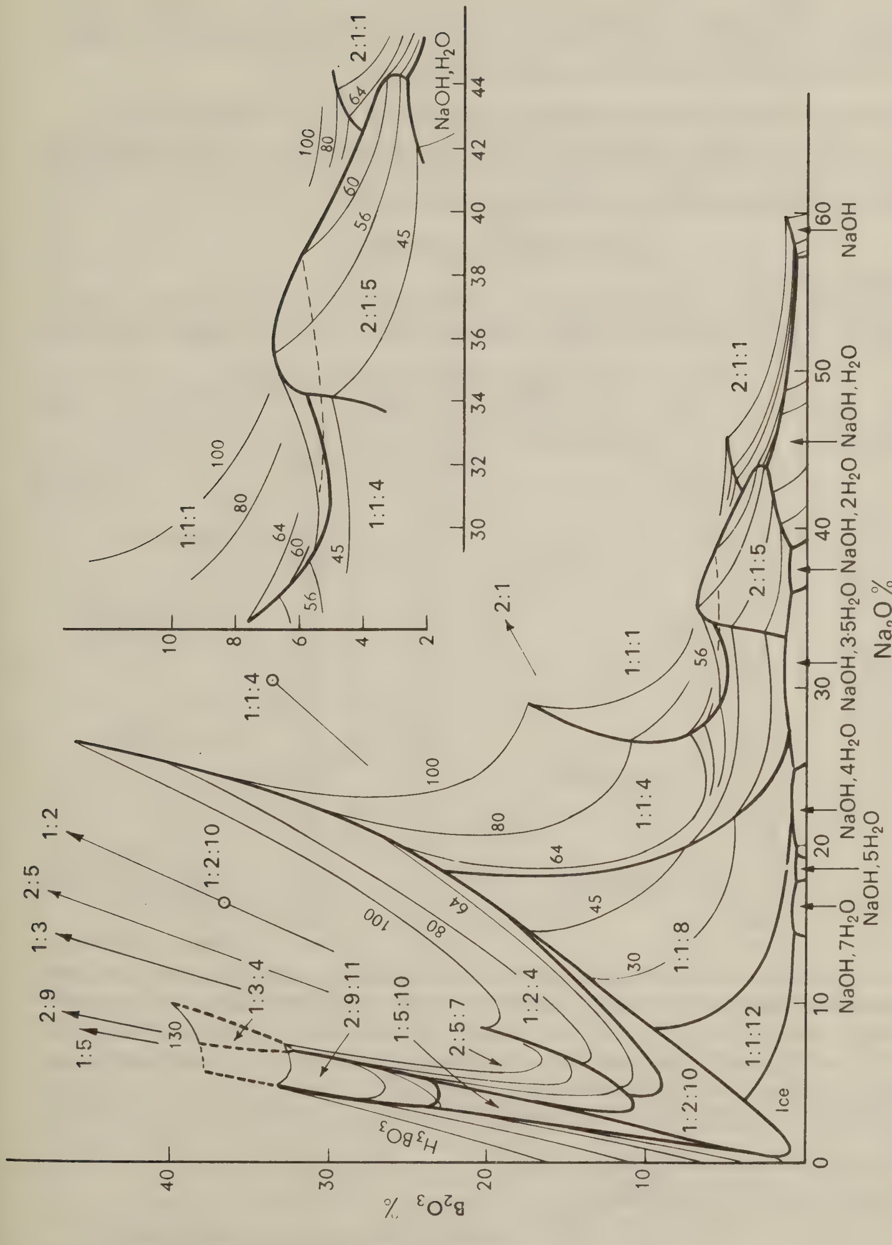

FIG. 3.—Phase diagram for the system Na$_2$O–B$_2$O$_3$–H$_2$O, 0–100°C[421A]

Tetrasodium Diborate Hydrates

TETRASODIUM DIBORATE PENTAHYDRATE, $Na_4B_2O_5,5H_2O$ OR $2Na_2O,B_2O_3,5H_2O$

The 2:1:5 compound crystallizes easily from solutions containing about 34 to 44% of Na_2O at temperatures from about 25–64°C. Its solubility is incongruent.[421] Its *X*-ray diffraction pattern has been published.[421,471A] In a thermogravimetric study, the water content remained at 5 molecules between 75° and 90°C, then decreased to 1 molecule at about 125°C and remained at 1 molecule until about 250°C. At 270°C the material became practically anhydrous.[421,471A]

TETRASODIUM DIBORATE MONOHYDRATE, $Na_4B_2O_5,H_2O$ OR $2Na_2O,B_2O_3,H_2O$

The 2:1:1 compound exists in equilibrium with solutions in the Na_2O–B_2O_3–H_2O system at temperatures as low as about 52°C and it has a large range of stability[705] at 100°.[421] Its *X*-ray diffraction pattern has been published.[421]

Sodium Metaborate Hydrates

SOLUBILITY VALUES

Solubilities (wt-% $NaBO_2$) in the $NaBO_2$–H_2O system have been determined[560,619,619A] and are recorded in Table IV and Fig. 4. A diagram has been published showing solubilities from 80° to 350°C, determined under pressure.[844A] In using values given in Table IV it should be noted that at temperatures below 11·5°C $NaBO_2,4H_2O$ is metastable with respect to $NaBO_2,6H_2O$, which ordinarily does not appear; if the solution is in equilibrium with $NaBO_2,6H_2O$ the solubilities are lower.[471A] Values taken from published solubility curves[471A] (wt-% $NaBO_2$) are:

Table IV.—The System Sodium Metaborate–Water

Temperature, °C	wt-% $NaBO_2$	Solid phase(s)	Temperature, °C	wt-% $NaBo_2$	Solid phase(s)
−0·511	1·011	Ice	30	23·6	$NaBO_2,4H_2O$
−0·850	1·731		35	25·6	
−1·286	2·695		40	27·9	
−2·148	4·853		45	30·8	
−2·532	5·732		50	34·1	
−3·174	7·317		53·6	36·9	$NaBO_2,4H_2O$ and $NaBO_2,2H_2O$
−4·084	9·511		55	37·2)	$NaBO_2,2H_2O$
−4·632	10·74		60	38·3	
−4·822	11·15		65	39·5	
−5·233	12·02		70	40·9	
−5·524	12·61		75	42·2	
−5·724	13·01		80	43·7	
−5·77	13·10	Ice and $NaBO_2,4H_2O$	85	45·4	
			90	47·4	
0	14·5	$NaBO_2,4H_2O$	95	49·6	
5	15·7		100	52·4	
10	17·0		105	56·0	$NaBO_2,2H_2O$ and $NaBO_2,0{\cdot}5H_2O$
15	18·5		110	55·8	$NaBO_2,0{\cdot}5H_2O$
20	20·0		115	55·5	
25	21·6		120·2	55·3	$NaBO_2,0{\cdot}5H_2O$ (b.p.)

Temperature, °C	Solubility	Solid phase
−3	8·25	Ice and $NaBO_2,6H_2O$ (cryohydric point)
0	10·0	$NaBO_2,6H_2O$
5	13·1	$NaBO_2,6H_2O$
10	16·8	$NaBO_2,6H_2O$
11·5	~17·4	Transition, $NaBO_2,6H_2O \rightarrow NaBO_2,4H_2O$

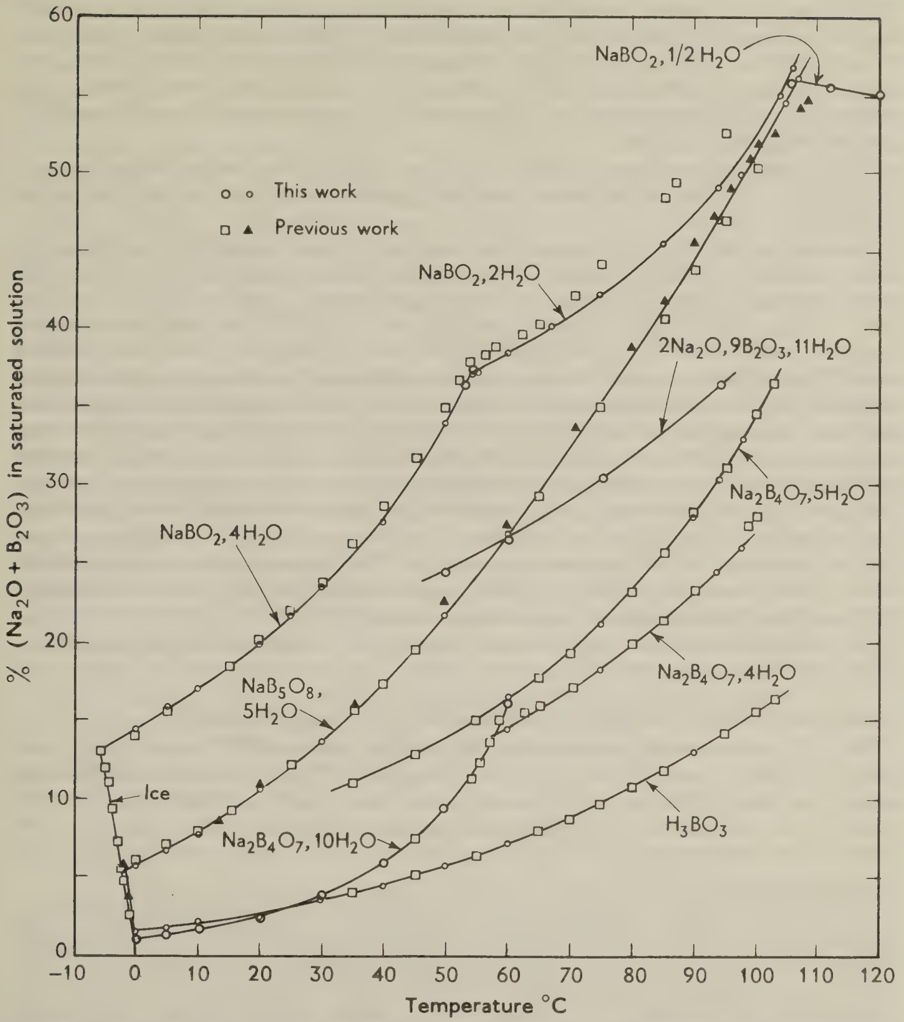

FIG. 4.—Solubility–temperature curves for boric acid, borax, sodium pentaborate and sodium metaborate[619]

Some previous solubility values[93, 1082] for sodium metaborate are believed to be somewhat high, probably because of the presence of silica or carbonate which appreciably increase the apparent solubility.

SODIUM METABORATE HEXAHYDRATE, $NaBO_2,6H_2O$ OR $Na_2O,B_2O_3,12H_2O$

The 1:1:12 compound was discovered in 1969.[471A] No *X*-ray diffraction pattern has been published. It crystallized in large transparent crystals when a solution of $Na_2B_2O_4,8H_2O$ was seeded at 0°C.[471A] Three or four days were required for equilibrium to be reached. Seed crystals were prepared by keeping a mixture of $Na_2B_2O_4$,$8H_2O$ and water at −25°C for a month. Solubility isotherms[471A] show that the 1:1:12 compound is stable in contact with its solution from −3° to 11·5°C. Solubility data are given in the previous paragraph.

SODIUM METABORATE TETRAHYDRATE, $NaBO_2,4H_2O$ OR $Na_2O,B_2O_3,8H_2O$

The 1:1:8 compound, triclinic, *d* 1·743 g ml^{-1} [560], hardness 2–3 on the Mohs scale, is the stable phase in contact with its saturated solution between 11·5° and

53·6°C and is the usual phase observed down to its cryohydric point at $-5{\cdot}77$°C.[560] Its *X*-ray diffraction pattern has been published.[107] The crystal structure, indicated by the formula $NaB(OH)_4,2H_2O$ has been determined by direct methods and consists of discrete tetrahedral $B(OH)_4^-$ groups and sodium ions coordinated octahedrally with H_2O molecules and OH groups.[95] The infra-red[391] and Raman[617A] spectra have been studied.

Solubility data are given in Table IV. In a study of the rate of dissolution of $NaBO_2,4H_2O$ by the revolving-disc method, sodium oxide was leached out of the surface.[679]

The relative humidity over a saturated solution of sodium metaborate at temperatures from 14° to 24°C is $90 \pm 1\%$.[560] The equilibrium relative humidity (which is readily reached) over a mixture of $NaBO_2,4H_2O$ and $NaBO_2,2H_2O$ is 39% at 19·3°C, 42% at 22°C, 43% at 24·8°C, and 45% at 27·0°C.[560] From the corresponding vapour pressures, the heat of hydration per mole of water has been calculated to be 12·55 kcal. When the 1:1:8 compound is dehydrated at room temperature over sulphuric acid or phosphorus pentoxide, the $NaBO_2,H_2O$ composition is approached without a slowing at the $NaBO_2,2H_2O$ composition.[559] Rapid dehydration by heating causes puffing, but this does not occur if a small amount of sodium hydroxide is added. The DTA curve shows endothermic effects with minima at 60° to 75°, 170°, 290° and 965°C which are attributed to the fusion of $NaBO_2,4H_2O$, $NaBO_2,$-$2H_2O$, $NaBO_2,0{\cdot}5H_2O$ and the anhydrous salt, respectively.[804] Solidification and swelling occurred at 165° in these experiments. The thermogravimetric curve shows a loss of 0·5 molecule of water at 130°C, two molecules at 140°, three molecules at 280°, and the last molecule at temperatures up to 800°C.[804]

The electrical resistance–temperature curve shows a sharp loss in conductivity between 38° and 140°C.[804]

SODIUM METABORATE DIHYDRATE, $NaBO_2,2H_2O$ OR $Na_2O,B_2O_3,4H_2O$

The 1:1:4 compound is triclinic, with specific gravity 1·909[560] and Mohs hardness 2–3. The crystallography has been studied[437, 560], and the *X*-ray diffraction pattern has been published.[437] Infra-red studies have confirmed that the tetrahedral $B(OH)_4^-$ ion is present.[315, 392] The specific magnetic susceptibility of the 1:1:4 compound and of the anhydrous salt have been found to be 0·511 and $0{\cdot}477 \times 10^{-6}$ c.g.s. units, respectively.[663]

The solubility data in Table IV and Fig. 4 indicate that the 1:1:4 compound is the stable phase in contact with a saturated solution from 53·6° to 105°C. In other heating-curve and solubility experiments, under pressure, it changed at 112°C to the 1:1:1 compound, which further changed to the anhydrous salt at 306°C in contact with its solution.[844A] Earlier work, starting with partially dehydrated $NaBO_2,4H_2O$, had given an endothermic effect at 155°C. This effect had been attributed originally to decomposition of a 1:1:2 compound, $NaBO_2,H_2O$[108, 695], but it is now attributed to experimental error.[844A] This 1:1:2 compound had been regarded as a stable phase at 100°C in solutions with $Na_2O:B_2O_3$ molar ratios of 1·8 to 3·2.[106] However, it was not found in later work[421A, 471A, 619, 619A, 844A] or in earlier work.[560, 730, 732] An *X*-ray diffraction pattern attributed to it[107] appears to be largely that of $Li_2B_2O_4,4H_2O$. The published evidence for the existence of a 1:1:2 compound, therefore, seems unconvincing.

The 1:1:4 compound crystallizes in very small needles, difficult to separate from the mother liquor, when a concentrated solution is rapidly cooled; however, larger plate-like crystals can be grown by heating the solid in its mother liquor at temperatures between 54° and 80°C for several days.[1053, 1068]

Dehydration

The 1:1:4 compound loses water very slowly at room temperature; when heated in an oven, it becomes sticky.[560] A study of its isobaric dehydration at 10 mm pressure indicated that 'roasting' at 75° to 80°C would increase its vapor pressure. At about 56° an amorphous product was obtained having the composition 1:1:1·8.

The end-product of the isobaric dehydration at 66°C, having the composition $Na_2O,B_2O_3,1{\cdot}22H_2O$, contained crystals which were identified as a 1:1:1 compound.[560] From the isobaric dehydration an approximate heat of dehydration was calculated to be 13·9 kcal mole^{-1} of water.[560] Another crystalline phase, regarded as another form of the 1:1:1 compound, having a different *X*-ray diffraction pattern, was produced by dehydrating the 1:1:4 compound to less than two molecules of water over phosphorus pentoxide, at room temperature and then dehydrating rapidly to the 1:1:1 composition by heating to 200°C in the open or to 120°C *in vacuo*. Further dehydration, at 350°C in the open or at 170°C *in vacuo*, produced the anhydrous salt, as indicated by its *X*-ray pattern.[560] When heated *in vacuo*, the 1:1:4 compound was stable up to 110°C; between 110° and 130°C half of the water was lost, and the last two molecules between 130° and 150°C.[307]

SODIUM METABORATE HEMIHYDRATE, $NaBO_2,0{\cdot}5H_2O$ OR Na_2O,B_2O_3,H_2O

The 1:1:1 compound apparently exists in two forms, one prepared by slow dehydration and heating to 100°C and the second prepared by rapid dehydration at 120° *in vacuo* or by heating a material having less than one mole of water per mole of $NaBO_2$ at 200°C in air.[560] Either form may be crystallized separately from highly alkaline solutions by seeding.[560] When both forms are present in contact with highly alkaline solutions at 60°C, the first form is converted into the second.[560] One form has been found to crystallize from its own solution at temperatures from 105°C to the boiling point.[619, 619A] Its *X*-ray pattern has been published.[1114A] Solubility and thermal analysis studies under pressure indicate that a 1:1:1 compound is formed at 112°C in contact with its solution and is in equilibrium with its solution up to 306°C, where it is converted to the anhydrous salt.[844A] The 1:1:1 compound can be dehydrated to a water content of about 0·2 molecule at 350°C in several days or to 0·1 molecule *in vacuo* over phosphorus pentoxide at 170°C, forming the crystalline anhydrous salt. Practically complete dehydration occurs at 500°C.[560] More recent research suggests that the 1:1:1 compound is in fact 3:3:2, with a crystal formula $Na[B_3O_5(OH)_2]$.[1258]

Disodium Tetraborate Hydrates

SOLUBILITY

A diagram based on solubility and thermal analysis studies has indicated that the 10, 5 (metastable), 4, 2, and 1 hydrates of borax can exist in equilibrium with their solutions[1203] under pressure at temperatures up to 387°C. There are temperature ranges above 95°C and above 130°C in which the 1:2:4 compound is metastable with respect to the 2:5:5 compound and unidentified spherulites, respectively. Solubility information is given in Table V and Fig. 4 for the 1:2:10 and 1:2:5 compounds; data for the 1:2:4 compound appear in Fig. 4 and later in this Section in Table VIII.

BORAX, DISODIUM TETRABORATE DECAHYDRATE, $Na_2B_4O_7,10H_2O$ or $Na_2O,2B_2O_3,10H_2O$

The 1:2:10 compound, specific gravity 1·715[1113], is monoclinic. Unit-cell dimensions[571, 834A] and indexed *X*-ray powder patterns have been established.[166, 834A] The borate ion in borax is a discrete eight-atom B–O ring (Fig. 5), composed of two BO_3OH and two BO_2OH groups and bridged by an oxygen atom.[584] A refinement of the structure verified that hydrogen bonds link the borate polyions into infinite chains and link these chains to the hydrated sodium-ion chains.[274] Two of the ten water molecules, therefore, exist as hydroxyl groups, and the structure is better represented by the formula $Na_2B_4O_5(OH)_4,8H_2O$. Some earlier work on the borax structure is regarded as incorrect.[852–4] The mineralogical properties of borax have been summarized.[1113] N.m.r. studies confirm the presence of boron in both 3- and 4-coordination[119, 212, 362], agreeing with the *X*-ray structure and showing that the sodium ions occupy two unique sites.[187] Proton magnetic resonance spectra have been recorded from $-196°$ to 46°C[535] and agree with the *X*-ray structure.[212]

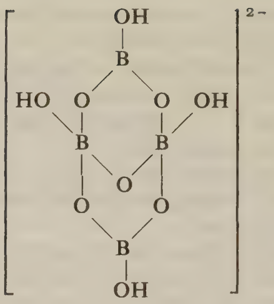

FIG. 5.—Structure of the borate ion in borax[274, 584] and tincalconite[1259]

Quadrupole coupling constants have been studied.[1156] Deuteron resonance studies show that there is molecular motion in deuterated borax at room temperature.[721] Studies have been made of the Raman spectra[438, 617A], which indicate the presence of hydroxyl groups, and the infra-red spectra.[568, 638, 880, 898, 1079] A review exists on the relation between the infra-red absorption spectra of borates and their structure.[661A] Structures of the free radicals produced in borax by irradiation with an electron beam at −196°C have been studied by ESR spectra.[605]

Borax shows both electronic and protonic conductance. At 15°C, conduction in borax pellets is only electronic, but at 35°C the mechanism involves proton conductance[533], which does not occur below about 21°C. There is a marked anisotropy in electrical conduction, the *b*-axis being the most favourable for protonic conduction[534]; an n.m.r. study provided information on the mechanism of proton conduction.[1178] The electrical conductivity of borax is 10^{-6} to 10^{-9} $\text{ohm}^{-1}\,\text{cm}^{-1}$ and the temperature coefficient is positive[363], the conductivity reaching maxima at 100°, 140°, 180°, and about 520°C.[812] The conductivity decreases with the loss of the last molecule of water at 350°C.[216]

The dielectric dispersion at low frequencies (0·001 to 1 Hz) and the effect of thickness and temperature on the permittivity of borax have been measured.[285A, 1243] The dielectric constant of borax–oil mixtures at various concentrations has been measured at room temperature (at 2×10^{-6} Hz) and the dielectric constant for borax was calculated to be 6·00. When the salt was dehydrated to a water content of two molecules the dielectric constant became 7·44.[136] Experimental values for the 'dielectric constant' for loosely packed borax powder in air, at 15°C and 1100 Hz, are[830]:

Bulk density, g ml^{-1}	0·6327	0·7026	0·7709
Dielectric constant	5·5	6·42	7·07

Measurements at 0·1 to 10 Hz and 0·06 to 300 kHz indicated that the dielectric constant is proportional to crystal thickness.[864] Alternating current and direct current polarization effects in borax have been studied by dielectric measurements.[865]

Values of the specific magnetic susceptibility of borax (decahydrate) and of borax dehydrated to 3, 2, 1, and 0 molecules water content are −0.591, −0·515, −0·491, −0·463, and $-0{\cdot}423 \times 10^{-6}$ c.g.s. units, respectively.[662–3]

The cracks produced in the faces of borax crystals by light percussion with a needle point have been studied.[460]

The packing of borax powders has been investigated. Particles 160 to 800 microns in size have about the same loose-packed bulk density, but the bulk density decreases as the particle size decreases below 160 microns. There is a correlation between angle of repose, sliding angle, and porosity.[351] The flow rate of borax powder decreases if the particle size is reduced below 160 microns. Below 100 microns, the particles do not flow.[380, 381–2] When the particle size is above 160 microns the angle of repose gradually increases as the particle size falls; it increases much more rapidly when the particle size falls below 160 microns.

The specific heat of borax has been determined as 0·385 at 25–50°C[737], in agreement with the previous value (Mellor, V, p. 72).

The integral heat of solution of borax (decahydrate) has been determined as follows[737]:

Temp., °C	Wt-% $Na_2B_4O_7$ in solution	Integral heat of solution g cal g^{-1} $Na_2B_4O_7$	Specific heat of solution g cal deg^{-1} g^{-1} solution
32	1	117·90	0·987
30	2·5	115·3	0·975
50	3·8	113·01	0·965
45	5·0	113·02	0·956

At 17·5°C, one mole of borax decahydrate, dissolved in 2310, 3025, 3740, and 4233 moles of water to give solutions containing 0·48, 0·37, 0·30, and 0·26 wt-% of $Na_2B_4O_7$ gave heats of solution of 128·7, 129·7, 130·3, and 130·9 g cal g^{-1} of $Na_2B_4O_7$, respectively.[646]

Solubility

Several solubility studies of the borax 5- and 10-hydrates have been made[70, 93, 561, 619, 619A]; data are presented in Fig. 4 and in Table V, which records values considered to be the best.[619] Borax decahydrate melts to a liquid phase under pressure, not far below 125°C[561]; the pentahydrate melts at 140°C.[70] The freezing point of a 1% borax solution has been determined as 0·25°C.[347] The decahydrate–pentahydrate transition point, 60·6–60·8° [93, 561], in the $Na_2B_4O_7$–H_2O system is lowered by addition of boric acid or sodium hydroxide.[619] In solutions saturated with sodium sulphate it is 49·3°C (ref. [1083], No. 21, p. 660); with sodium chloride, 39·6°C; in solutions saturated with sodium and potassium chlorides and potassium sodium sulphate 35·5°C[114], and in liquor formed by evaporation of Searles Lake brine, 30° to 32°C.[956] At temperatures above the transition point, borax decahydrate will readily dissolve with crystallization of the pentahydrate. Below this point the reverse process will occur and can be observed easily under a microscope at room temperature.[557]

Table V.—Solubility of Borax in Water

(Values are expressed throughout in wt-% of $Na_2B_4O_7$)

Temperature, °C	Solubility	Solid phase(s)	Temperature, °C	Solubility	Solid phase(s)
−0·42	1·03	Ice and $Na_2B_4O_7,10H_2O$	60	16·00	$Na_2B_4O_7,10H_2O$
0	1·05	$Na_2B_4O_7,10H_2O$	60·8	16·65	$Na_2B_4O_7$,10 and $5H_2O$
5	1·30		60	16·35	$Na_2B_4O_7,5H_2O$
10	1·63		65	17·88	
15	2·00		70	19·49	
20	2·48		75	21·20	
25	3·06		80	23·38	
30	3·80		85	25·60	
35	4·76		90	28·06	
40	5·92		95	31·10	
45	7·50		100	34·63	
55	9·45		102·8	36·73	$Na_2B_4O_7,5H_2O$ (b.p.)
55	12·25				

The solubility of borax at 20°C has been reported as 89·36 g per 100 g of 86·5%

glycerol and 111·15 g per 100 g of 98·5% glycerol.[340] At 25°C its solubility in ethylene glycol is given as 41·6% by weight; in diethylene glycol, 18·6%; in methanol, 19·9%; in acetone, 0·6%; and in ethyl acetate, 0·14%. In 46·5% ethanol by volume at 15·5°C, the solubility is 2·48%.[1201]

The vapor pressure of borax solutions at 9–17°C is very close to that of pure water.[564] Borax is not hygroscopic at 78% relative humidity at 20°C.[13]

The rate of solution of borax, studied by the revolving disk method at 25–40°C, increases linearly with the square root of the angular velocity, agreeing with theoretical values for diffusive dissolution. At 0–10°C the rate of dissolution was less than theoretical, indicating mixed kinetic and diffusive dissolution.[679] The etch figures correspond to the theoretical liquid-flow lines.[679] The rate of dissolution was also studied in a layer of crystals suspended by a stream of water at 10–30°C.[680] Etch figures, obtained by using distilled water as the etching agent, have confirmed that borax is monoclinic.[289]

The rate of dissolution of borax in 20–79% aqueous dioxan solutions at 30–50° has also been studied.[602]

Crystallization

Borax crystallizes from aqueous solutions as monoclinic prisms. Its crystal habit has been studied under various conditions of supersaturation, pH, presence of nucleation retarders, sludge density, and slow and 'flash' crystallization.[270] The nucleation rate is independent of supersaturation but proportional to the solids concentration and inversely proportional to the temperature. A particle size smaller than about 45 mesh is produced by crystallizing at an optimum temperature between 27°–43°C in a slurry containing 250–500 g of borax crystals per litre; a larger particle size is produced at higher temperatures, e.g., 49–55°C, with 50 to 250 g of borax crystals per litre.[972] Fatty acids have an undesirable effect on the crystal habit of borax and may be precipitated by treatment with a quaternary ammonium compound and removed by filtration.[969A] A process for producing single-crystal borax from solution by using a low supersaturation in the presence of seed has been patented.[1192] The growth of borax crystals is affected by dyes, and the effects of a number of dyestuffs have been tabulated.[129] From aqueous or alcoholic solutions borax is deposited in rings round the containing vessel[235]; this is thought to be due to better wetting of the crystals than wetting of the glass by the evaporating liquid.[253] The mechanism of inclusion by growing borax crystals of oil drops from emulsions has been studied. The form and nature of the inclusions depends on wetting of the crystal face by the oil.[415]

Dehydration

Borax dehydration follows two different courses, stable or unstable, depending on whether or not it has been heated to 50°C.[564] An unheated, freshly crystallized decahydrate follows the unstable dehydration. It has a vapour pressure of only 1·6 mm at 20°C and 1·9 mm at 25°C and becomes amorphous when dehydrated over sulphuric acid at room temperature, the last of the decahydrate crystals disappearing at a water content of about two molecules.[564] After the borax has been heated to 50°C, however, it follows the stable dehydration. In this case its vapour pressure at 19·8°C is 10 mm, and it can be reversibly decomposed to the crystalline pentahydrate at this pressure and temperature.[564] Long storage times can also apparently produce the stable dehydration. Display specimens of borax decahydrate crystals, after 10 years of open exposure, have changed to microcrystalline pentahydrate with a water content of 4·7 molecules but have retained their original shapes.[564]

Borax which had been crystallized by cooling its solution quickly from 40° to 10°C was partially dehydrated over phosphorus pentoxide at room temperature and atmospheric pressure. During the dehydration unchanged crystals and an amorphous phase containing on the average 2·6 molecules of water, were present, as shown by quantitative *X*-ray diffraction.[88] At 45° and about 0·1 mm Hg the loss in water was eight molecules, agreeing with the structure of borax. Isothermal studies of the rate of dehydration of single crystals at 0·002 Torr at temperatures from 19° to 46·5°C also resulted in a practically amorphous product containing 2 molecules of water.[834A] The mean value of the activation energy for the dehydration process was 12 kcal mole^{-1}. The effect of pressure has been investigated recently.[1174] The mechanism of dehydration and rehydration with deuterium oxide vapour has been studied by means of proton magnetic resonance.[88]

The vapour pressure over a mixture of the pentahydrate and decahydrate has been measured at 15–25°C and 58–59°C.[561, 564] From these values the heat of dehydration of the decahydrate to form the pentahydrate and water vapour, per mole of water vapour, was calculated to be 12,942 g cal.[561] By plotting these vapour pressure values, a curve was obtained from which the following values were read:

Table VI.—Water Vapour Pressures over Mixtures of $Na_2B_4O_7,10H_2O$ *and* $5H_2O$

Temperature, °F	32	40	50	60	70	80	90	100	110	120	130	140
Temperature, °C	0	4·4	10	15·6	21·1	26·7	32·2	37·8	43·3	49·9	54·4	60
Vapour pressure mmHg	2·7	3·6	5·2	7·5	10·8	15·6	22·6	32·6	47	68	99	141
Relative humidity, %	59	57	56·5	56·6	57·6	59·5	62·6	66·5	71·3	77·7	86·2	95·1

The vapour pressures over a mixture of borax decahydrate and kernite ($Na_2B_4O_7,4H_2O$) at 19·8° and 58·2°C are 10·3 and 131·0 mm, respectively.[561] As these pressures are lower than the pressures of a mixture of borax pentahydrate and kernite, which are 11·9 and 151·8 mm, respectively at these temperatures[561], the pentahydrate is metastable and should disproportionate to form a mixture of kernite and borax in this temperature range. However, this reaction does not occur in the absence of a solution in equilibrium with both kernite and borax. From these values the heats of dehydration to water vapour have been calculated, per mole of water, to be[561]: 10 → 4 hydrate, 12,924 g cal; 5 → 4 hydrate, 12,834 g cal.

Differential thermal analysis studies of borax by several investigators have shown endothermic peaks at (i) 60°, 105–110°, and 160–170°C[11]; (ii) 120°, 160°, and 730°C[812]; (iii) 50° (small peak) and 100–220°C (large peak)[166]; (iv) 75°, 162°, and 202·5°C[195–6]; (v) 86°, 131°, and 176°C[325]; and (vi) 70°, 110°, and 145°C.[383] *X*-Ray diffraction studies of borax heated to temperatures from above 50° to 320°C showed the presence of pentahydrate. The sample was amorphous, as indicated by the presence of diffuse bands, from 320° up to about 675°C, the temperature at which it crystallized.[195–6] Some studies have shown an exothermic peak at 50°[195–6] or 75°C.[11] This peak may be related to the change which occurs when borax is heated to about 50°C, after which it will follow the stable dehydration and form the pentahydrate (*v. supra*).

An early review[676] on the dehydration of salt hydrates includes reference to borax. A thermogravimetric curve has been determined and the products of dehydration with infra-red radiation have been compared with those obtained in a desiccator at 105–130°C.[577]

The velocity of water molecules leaving borax during dehydration has been measured by means of a torsion balance and microbalance. The heat of hydration of borax was calculated from these measurements to be 38·5 kcal mole^{-1} of $Na_2B_4O_7$[664], which compares favourably with the literature values 36·1[664], 34·1 (Mellor, V, 72), and 32·4 kcal[737] for the reaction $Na_2B_4O_7(c) + 10H_2O(l) = Na_2B_4O_7,10H_2O(c)$. Products have been prepared from borax over sulphuric acid at known vapour pressures, and in a current of dry air at various temperatures, containing 4, 3, 2, and 1 molecule of water.[236] The molecular volume of water in these products was about 14 cm^3 mole^{-1}.[236] The kinetics of dehydration of borax powder in a nitrogen stream at 50–60°C, and of single crystals *in vacuo*, have been studied, and equations developed to represent the rates.[595] Samples of borax decahydrate, after heating to constant weight in an oven at 80°, 100°, and 200°C, contained 3·4, 1·8, and 1·1 molecules of water, respectively.[546] The sample heated at 100°C was largely amorphous; the samples heated at 80° and 200°C contained some pentahydrate. A sample dehydrated at about 25°C over calcium chloride for five weeks to a water content of 4·5 molecules still contained some unchanged decahydrate.[546] In another thermal dehydration study, borax was stable up to 35–38°C, and lost half its water when heated to 108°C. Four more moles of water were lost up to 172°C, and a temperature of 500–525°C was necessary to get constant weight.[222] When borax was heated at 180°C to constant weight, nine molecules of water were lost.[675] When borax is heated rapidly, it melts before dehydration; in an electron microscope, spherical drops are formed.[720] Slow dehydration of borax results in the loss of eight molecules of water between 50° and 150°C[726], or 50° and 110°C[166], and the last two molecules are lost below about 400°C. In other work, eight molecules of water were lost at 60–140°C and the last two molecules were lost gradually between 145° and 290°C.[383] A summary[812] of other work gave the remaining water as five molecules at 80°, three molecules at 100°, one molecule at 140°, and 0·6 molecule at 300°.

When borax pentahydrate or decahydrate is dehydrated rapidly by heating, the particles puff to several times their original size.[151, 1183] 'Puffed' borax can have a void volume as high as 90% and thus can be loaded with large amounts of organic liquids and solids[684], such as surfactants and chlorinated hydrocarbons.[152] Calcined borax containing five molecules of water or less, or other sodium borates not containing seeds of $Na_2B_4O_7,10H_2O$, when mixed with boric acid, will dissolve in water without heating to give a solution supersaturated with borax.[977]

Borax has been dehydrated by heating with hot air in a fluidized bed. The water content is reduced to 10–20 wt-% at 100–200°C. The temperature is then increased to 220–700°C to give 98–99·8% $Na_2B_4O_7$.[1077] When heated under reduced pressure, borax loses its water without appreciable change in its particle size or shape. Curves showing the water loss *versus* time at 40 mm pressure indicate that at 110°C six molecules were lost in 4 h and at 360°C 9·8 molecules were lost in less than an hour.[1028A] A curve showing the dehydration of borax *in vacuo* indicates that eight molecules of water are lost between about 20° and 70°C. The last two molecules are lost gradually at temperatures up to 350°C.[304–5, 307] In other studies *in vacuo*, seven molecules of water were lost between 35° and 78°C[595], and eight molecules were lost rapidly at 60°C.[305] Distillation with organic solvents removed somewhat more water from borax than heating in an oven at the same temperature. Curves showing the water lost as a function of the amount of solvent distilled, with benzene (80°), toluene (110°), xylene (138°), and petroleum (165–170°C) reach maxima at about 5·3, 6·9, 7·8 and 8·3 molecules respectively, compared with losses of 2·9, 5·9, and 7·1 molecules in an oven at the first three temperatures.[614] This behaviour agrees with the existence of two molecules of water in borax as hydroxyl groups. Conversion of the decahydrate to the pentahydrate by distillation with xylene required a heat input of 2130 g cal g^{-1} of water.[614] In another study, refluxing with 15 parts of absolute or 95% alcohol for 2 h removed 6·3 molecules of water from borax, and repeated heating increased the loss to 7·2 molecules.[672] Heating for 3 h on a water bath removed five molecules[671], as did standing over sulphuric acid.[673] Cold 95% alcohol has no effect on borax.[672, 674] The heat of formation of the decahydrate was calculated in 1952 to be $-1497{\cdot}2$ kcal $mole^{-1}$.[1118]

Chemical Reactions

Borax may be readily prepared with the theoretical water content by washing the crystallized material with several portions of alcohol and then with ether, and it has been recommended as an acidimetric standard.[346A, 77] When crystallized at temperatures below 55°C, washed twice with water and twice with acetone and air-dried overnight, the water content of a sample of borax was 9·985 molecules.[575] The water content may be maintained at exactly ten molecules by storing borax over a solution saturated with both sucrose and salt.[564] A review has appeared on the preparation, properties and application of borax as a primary standard.[691A] A comparative study of borax and sodium carbonate as acidimetric standards has been made[913] indicating that borax is more suitable.

Damp borax, heated in a closed container at 98°C in the presence of kernite seed, is converted to kernite ($Na_2B_4O_7,4H_2O$) in 24 to 48 h.[1062]

Borax reacts with boric acid in a closed container at 120°C[990, 990A] to form a sodium polyborate product having advantages as a component in a glass batch. Borax–boric acid mixtures, heated to 140–200°C in a suitable temperature cycle, form non-hygroscopic polyborate products containing 5–12% of water which, when used in glass batches, decrease the loss of borate during melting.[1032] DTA and thermogravimetric curves for a mixture of one molecule of borax and two molecules of boric acid have been published.[903] A break occurred in the curves at the composition $Na_2O,3B_2O_3,2H_2O$. Dehydration in an autoclave at 120–170°C also resulted in a product of this composition, which had an *X*-ray diffraction pattern different from those of the starting materials and their dehydration products.[903] The infra-red absorption spectrum of this material showed the OH band at 3600 cm^{-1} but not the H_2O band at 1650 cm^{-1}.

When borax crystals are washed with a boric acid solution, sodium pentaborate may form when the adhering liquor evaporates. The resulting coating of pentaborate on the surface of the borax crystals inhibits caking.[969]

Calculations have been made for a cyclic process in which borax pentahydrate and carbon dioxide would react when dissolved under pressure to produce sodium bicarbonate and boric acid.[1043]

Borax is converted to sodium sulphate when contacted with a gas containing superheated steam and sulphur trioxide at a temperature above 185°C. Boric acid can be recovered from the effluent gas.[1040] Borax pentahydrate or decahydrate mixed with sulphuric acid gives a furnace feed which when melted gives two liquid layers. The upper layer may be separated and cooled to give a product containing about 96% of B_2O_3. The lower layer is sodium sulphate containing a small amount of excess sulphur trioxide.[1033, 1046, 1049, 1052, 1054, 1054A, 1071, 1075–6] Borax pentahydrate or anhydrous borax reacts with spent alkylation sulphuric acid at 100–120°C to give a dry, black, granular material from which boric acid can be obtained by a cyclic process.[1125]

Borax or borax pentahydrate, dry-mixed with sodium hydroxide and fed to a heated drum dryer, forms flakes of sodium metaborate containing less than two molecules of water of crystallization per molecule of $NaBO_2$.[1067] If a sodium hydroxide solution is sprayed, sufficiently slowly for the mass to remain dry, on an agitated bed of borax pentahydrate or decahydrate, sodium metaborate is formed with a water content of one to four molecules per molecule of $NaBO_2$.[1065] Borax, when mixed with sodium hydroxide solutions containing the calculated amount of sodium hydroxide and water, forms at first a sticky, viscous mass; as mixing continues, a granular sodium metaborate is produced having two to four molecules of water per molecule of $NaBO_2$.[988] When the water content is 3·5 molecules, a plastic mass is formed at 75–105°C which can be flaked on a cooled drum.[1072]

A mixture of borax and calcium carbide produced only a small amount of acetylene at 100°C, indicating that only a trace amount of its water content reacted. With phosphorus trichloride at 15°C, 6% of its water content reacted to give hydrogen chloride; with acetyl chloride at 15°C, 11·22% of its water content reacted.[743] Borax does not react with powdered beryllium at temperatures up to 200°C, as do some other salt hydrates.[10] When mixed with each of the explosives cyanuric triazide, trinitrotriazidobenzene, and thallous azide, it increased the impact sensitivity.[112] Borax crystals will nucleate supersaturated solutions of sodium sulphate decahydrate and thus prevent undercooling of more than 2°C in a closed system.[831] Borax reacts with manganese ore, sugar, and sulphuric acid to produce $MnO,B_2O_3,2H_2O$; a process based on this reaction has been described.[718A] A powdered mixture of calcium fluoride and borax containing 62% of CaF_2 or less gave negative tests for fluoride after storage for one to three weeks, apparently on account of formation of fluoborate.[901] Borax, mixed with powdered magnesium, aluminium or lithium and ignited by means of a fuse, gives a brilliant yellow light.[950] With liquid ammonia, borax loses nine molecules of water and takes up some ammonia.[564] Ammonia gas removes most of the water.[564] The end products had the *X*-ray diffraction pattern of the pentahydrate.[564] In an ESR study of the pyrolysis of cotton cellulose in the presence of various flame retardants, free radicals became apparent at a higher temperature with boric acid or borax present than with the other salts tested.[39A] TGA and DTA studies of the effect of borax on the pyrolysis of wood have indicated glow suppression and a decrease in the height of exothermic peaks.[678A] Borax increased the amount of char and decreased the tar.[824]

Anhydrous or hydrated alkali-metal borates react with methanol to give methoxyborates. If the borate contains more boric oxide than the metaborate, trimethyl borate is also formed.[484] The *X*-ray patterns of $MB(OCH_3)_4$, where M = Li, Na, K or Cs, and of $LiB(OCH_3)_4,2CH_3OH$ have been published.[484] Borax will also react with carbon dioxide and methanol to form trimethylborate.[1152] Other alcohols and borates may also be used.[1026] Borax, partially dehydrated borax, or anhydrous sodium metaborate reacts with carbon monoxide at 600 lb in^{-2} (gauge) and 100°C in methanol solution to give sodium formate and methyl borate.[1127] Disodium tetraborate pentahydrate can be converted almost completely into sodium metaborate and trimethylborate by distillation of the trimethylborate–methanol azeotrope in the presence of sufficient excess methanol.[1128] Borax reacts with ethylene glycol (or other high-boiling alcohol) and ammonium sulphate or chloride, forming glycol borate, which can be trans-esterified to form methyl borate.[1150] By dissolving borax in glycols, polyhydric alcohols or a mixture of glycols and alcohols, and removing the water formed by vacuum distillation, condensation products are produced which inhibit corrosion in hydraulic fluids.[1198] Borax has been separated from a mixture of Glauber's salt, natron and sodium chloride by flotation.[1022A]

DISODIUM TETRABORATE PENTAHYDRATE, TINCALCONITE, $Na_2B_4O_7,5H_2O$ OR $Na_2O,2B_2O_3,5H_2O$

'Borax pentahydrate', specific gravity 1·880[1113], is rhombohedral, although the crystals often resemble octahedra. Interfacial angles have been measured.[636] Its mineralogical properties have been summarized.[1113] In nature, it is usually found as a fine-grained deposit formed by dehydration of borax in the atmosphere.[1113] Occasionally larger crystals are found, such as those from the lower part of Searles Lake.[114, 636] The *X*-ray pattern has been published[166, 636], and unit-cell data have been determined.[571] The structure is believed to contain the same discrete polyborate ion that occur in borax decahydrate[161–2], since a change in humidity will change borax pentahydrate to decahydrate, and vice versa, readily at room temperature (p. 364). Also, n.m.r. studies indicate that the same polyborate ion occurs in borax and in the pentahydrate[188, 362], as later confirmed by *X*-ray[1259] (Fig. 5). A structure published in 1948 is thus regarded as incorrect.[271]

The infra-red absorption spectrum has been determined.[898, 1079] Quadrupole coupling constants have been studied for borax, borax pentahydrate, and borax dehydrated to water contents of 3, 2, and $1H_2O$.[1156]

Proton magnetic resonance studies of tincalconite at $-153°$ to 80°C have led to the formula $Na_2[B_4O_5(OH)_4],3H_2O$, in agreement with dehydration experiments.[64]

The decahydrate–pentahydrate transition point in contact with a saturated solution is 60·6–60·8°C.[93, 561] This is lowered in the presence of other salts (p. 363). When a saturated solution is heated near the boiling point for a day or more, kernite crystals are formed.[561] The phase diagram (Figs. 1 and 2) and the solubility curves (Fig. 4) show that the pentahydrate is metastable at all temperatures. This has been expressed in schematic free energy–composition diagrams.[163] The pentahydrate, in contact with its aqueous solution, is metastable with respect to kernite above a temperature estimated at $39 \pm 5°C$.[561] The metastable solubility of the pentahydrate has been determined at temperatures up to the boiling point (p. 363), and further to 136°C, the transition point to the dihydrate, and to the congruent melting-point, 140°C.[70] At 25°C, the solubility of the pentahydrate has been determined as 11·7 wt-% $Na_2B_4O_7$ in methanol, 21·5 wt-% in ethylene glycol, 6·9 wt-% in diethylene glycol, and 15·1 wt-% in propylene glycol.[1117A]

The heat of formation of $Na_2B_4O_7,5H_2O$ has been calculated to be −1143·5 kcal mole^{-1}.[1118]

The specific heat of the pentahydrate has been determined as 0·315 g cal deg^{-1} g^{-1}.[737]

Values for the integral heat of solution of the pentahydrate are listed in Table VII.[737]

Table VII.—Integral Heat of Solution of Borax Pentahydrate in Water

Temp., °C	Wt-% $Na_2B_4O_7$ in solution	Integral heat of solution (g cal g^{-1} $Na_2B_4O_7$)
35	1·0	61·34
40	2·5	53·94
50	3·8	51·52
55	5·0	50·92
65	7·5	48·60
70	10·0	47·26
70	12·0	45·92
75	14·0	45·31
75	16·0	44·90
85	20·0	44·73
95	24·0	45·99
101	29·0	46·60

A Merkel enthalpy–concentration diagram for the system $Na_2B_4O_7$–H_2O from 0° to 100°C has been published.[737]

Dehydration

The water content of the 'pentahydrate' is usually 4·7–4·75 molecules. The reason that it is not exactly five is not known, but there is probably a deficiency in the bulk water content of the crystals rather than surface dehydration. A curve of composition as a function of temperature, at 10 mm pressure of water vapour, indicates that the water content decreases gradually from 5·0 molecules at 20°C to 4·6 molecules at 80°C.[564] At 88°C (again at 10 mm pressure) the water content changes reversibly from 4·5 to 2·3 molecules; still higher temperatures are necessary for further dehydration at this pressure.

Thermogravimetric curves show that three molecules of water are lost on heating to 140°C.[166, 64] The last two molecules are lost more slowly; the anhydrous product is reached at about 410°C. The DTA curve shows a very strong endothermic effect beginning at 120°C and reaching its maximum at 170°C[166], or beginning at about 100°C with a maximum at about 160°C.[11] Another study showed heat effects at 158°, 343°, 609°, and 642°C.[431]

Over phosphorus pentoxide in a desiccator, the pentahydrate loses water more slowly than the decahydrate, reaching a water content of four molecules, compared with 2·5 for the unheated decahydrate, 3·1 for the heated decahydrate.[564] In an oven, the pentahydrate reached the following compositions (expressed as molecules of water remaining)[564]:

Hours at 100°		150°	175°	190°C
2	4·22	1·74	1·51	1·36
6	3·70	1·64	1·48	1·32
14	3·44	1·57	1·49	1·28
126				1·11

Further heating decreased the water content (again, as molecules of water remaining) as follows: 42 h at 220°C, 0·74; 28 h at 250°C, 0·64; 24 h at 286°C, 0·31; 38 h at 294°C, 0·17; 19 h at 336°C, 0·14; 25 h at 450°C, 0·01.[564] The pentahydrate loses three molecules of water at 88°C at 2 mm pressure, or at 140°C in the air to give an amorphous dihydrate.[64] The same dihydrate is obtained by heating the pentahydrate in boiling xylene (136–139°C) for 6–10 h.[564] According to another investigation, three molecules are lost *in vacuo* at about 120°C[305] and the last two are gradually lost between 120° and about 350°C.[305, 307] Like borax, the pentahydrate puffs when heated rapidly. A 'puffed' product can be produced containing 1·2 molecules of water and having a bulk density of 0·042 g cm^{-3}.[1183]

Chemical Reactions

The pentahydrate is sufficiently soluble in methanol for the Fischer titration to correspond to the expected 12 molecules of water.[166] It reacts with concentrated sulphuric acid to form a mixture which will give two immiscible liquids when fused; a process has been developed in which the two layers are separated while molten to produce boric oxide and sodium sulphate.[266A]

When a mixture of boric acid and a hydrate of borax, having a molar ratio $Na_2O:B_2O_3 = 0{\cdot}2$, is added continuously to a slurry of sodium pentaborate, it dissolves rapidly with crystallization of further sodium pentaborate. Use of a calcined borax avoids accumulation of water in the solution.[1064]

Granular mixtures of disodium tetraborate pentahydrate with boric acid cake severely during storage, but a non-caking mixture can be made by moistening and drying at 70–115°C with agitation.[1059A] Mixed with boric oxide, the pentahydrate forms a water-soluble mixture having a bulk density of greater than 50 lb ft^{-3}.[1194]

Other reactions of the pentahydrate are mentioned under the decahydrate, pp. 367–8.

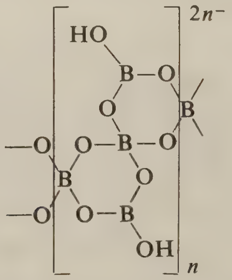

FIG. 6.—The borate polyion in kernite[164, 273, 275]

KERNITE, DISODIUM TETRABORATE TETRAHYDRATE, $Na_2B_4O_7,4H_2O$ OR $Na_2O,2B_2O_3,4H_2O$

Kernite, monoclinic, specific gravity 1·908[561, 1113], hardness 2·5, a striking mineral because of its cleavage and large crystal-size, was first described as orthorhombic.[734] Descriptions of the crystals have been published.[561, 734, 1113] Its unit-cell data[571, 709] and *X*-ray powder pattern[166, 546] have been determined. The structure (Fig. 6) contains parallel infinite chains of the polyion $[B_4O_6(OH)_2]_n^{2n-}$, which is composed of six-membered rings, each having one boron in trigonal coordination and two in tetrahedral coordination.[164, 273, 275] The charge distribution among the sodium, boron and oxygen atoms has been determined.[182A] The rings are joined by sharing tetrahedral boron atoms so that the plane of each ring is approximately perpendicular to the plane of the preceding ring of each chain. The chains can be regarded as formed by polymerization of the $[B_4O_5(OH)_4]^{2-}$ ions in borax, but the polymerization involves breaking a B–O bond[164, 275] and is not a simple elimination of water between hydroxyl groups, such as can be written for the formation of colemanite.[161] This structure agrees with the observed slow rate of crystallization[1062] and dissolution. It also explains the excellent cleavage and fibrous nature of kernite, as the bonds holding the neighbouring chains together are much weaker than the bonds in the chains.[275] It also agrees with the fact that the solubility curves of disodium tetraborate pentahydrate and kernite are more nearly parallel than are the solubility curves of different hydrates of other salts. This would seem to be likely as they are both trihydrates.[162] Some structures previously proposed[656, 656A, 657, 1078] are regarded as incorrect.

An n.m.r. study of kernite has indicated that two of the boron atoms are in trigonal coordination and two in tetrahedral coordination.[119] Another study indicated four non-equivalent ^{11}B sites.[895] The nuclear quadrupole resonance of ^{11}B in kernite has been studied.[308] The infra-red absorption spectrum[819, 880, 898, 1079] is different from those of borax decahydrate and pentahydrate.

The heat of formation of kernite at 24°C has been calculated to be $-1072{\cdot}9$ kcal mole^{-1}.[1118]

The solubility of kernite is lower than that of the pentahydrate (Fig. 4). Values are given in Table VIII.[619, 619A] Kernite is the stable phase in contact with its solution from 58·2°C to about 95°C.[619, 619A] At 94° it is the stable phase in solutions with molar ratios ($Na_2O:B_2O_3$) from about 0·5 to 0·74[619, 619A], but it usually does not appear when borax pentahydrate is crystallized. Its rate of crystallization, very slow compared to that of the pentahydrate, increases with temperature.[1062] It can be crystallized from borax solutions at temperatures up to about 130°C.[561] Solutions saturated with borax pentahydrate at 100°C, when seeded with kernite and cooled a few tenths of a degree per day, will grow kernite crystals several centimetres in length.[561] The rate of dissolution of kernite is also slow compared to that of borax pentahydrate or decahydrate. When 190 g of 'finely crushed' kernite was contacted with 500 ml of water at 85°C, 74·6% dissolved in 7 min, 91·5% in 15 min, and 96·6% in 40 min. Calcined kernite dissolves much more rapidly.[971] When a kernite melt was heated at 154°C overnight in a sealed tube and then kept for 12 days at 130–135°C, spherulites were formed with a $Na_2O:B_2O_3$ ratio lower than that in borax.[561] A heating curve of kernite in a sealed tube showed a well-defined break at 151·5°C, attributed to congruent fusion.[561] Thermal analysis and solubility determinations under pressure have indicated that kernite is in equilibrium with its solutions from 58° to 171°C.[1203] The solubility, vapour pressure and crystal structure of borax, borax pentahydrate and kernite have been discussed in relation to the formation of the kernite–borax deposit at Boron, California.[162] The effect of uniform pressure on the borax–kernite transition temperature has been calculated to be 0·015°C per bar.[162] In the Kramer deposit, the change of borax to kernite probably took place at about 48 ± 5°C at a depth of 2500 ± 500 ft.[162] The transition point of borax to kernite in contact with its saturated solution is 58·2°C[561]; in saturated sodium chloride solution it is about 41°C.[162]

Table VIII.—Solubility of Kernite, $Na_2B_4O_7,4H_2O$, in Water

Temperature, °C	Solubility, wt-% $Na_2B_4O_7$	Temperature, °C	Solubility, wt-% $Na_2B_4O_7$
58	14·20	80	19·72
60	14·67	85	21·28
65	15·81	90	22·96
70	17·02	95	24·75
75	18·31	100	27·23

Hydration and Dehydration of Kernite

At 86% relative humidity, powdered kernite absorbed 1·2 molecules of water in 9 days to form borax decahydrate. Hydration is slower at 75%, and at about 70%

relative humidity kernite required 40 months to take up 1·1 molecules of water, even though some borax was added.[561] Kernite does not hydrate to form the pentahydrate directly.[589] Kernite loses water slowly at room temperature over phosphorus pentoxide *in vacuo*, forming a crystalline dihydrate, 'metakernite', which will take up water at 60–70% relative humidity to form kernite again.[561, 562] Metakernite can also be formed by heating kernite at 100–120°C[561], and has been reported to crystallize from an amorphous $Na_2B_4O_7$–H_2O composition containing 83–91% of $Na_2B_4O_7$ under pressure at 240°C.[1203] The kernite–metakernite equilibrium gives a vapour pressure of 10 mm between about 85° and 94°C, but equilibrium is reached very slowly.[561]

The DTA curve for kernite has endothermic peaks at 185°C[11, 346, 588] or 188°C[431], and at 560°C[346] and an exothermic peak at 600°C.[346] In another study, there were peaks with maxima at 200° and 460°C.[166] Heating kernite for 12-h periods at successively increasing temperatures, with 30° intervals, gave a thermogravimetric curve showing an inflection at about 100°C corresponding to a loss of two molecules of water; the last two molecules were lost gradually at temperatures up to 370°C.[166] A dehydration curve for kernite heated *in vacuo* showed that dehydration began at about 60°C, with a rapid loss of about 32% of its water at temperatures below 80°C, and a loss of an additional 18% between 110° and 130°C; the last two molecules were lost gradually between 130° and 400°C.[304–5, 307]

The Fischer titration of kernite gave an apparent 11 molecules of water, as would be expected.[166]

DISODIUM TETRABORATE DIHYDRATE, METAKERNITE, $Na_2B_4O_7,2H_2O$ OR $Na_2O,2B_2O_3,2H_2O$

The dihydrate is the disodium tetraborate phase stable in contact with its solution under pressure from 161° to 260°C, according to solubility and thermal analysis studies under pressure.[1203] Its preparation and hydration are described under kernite (*v. supra*). If metakernite is heated to 190°C, half its water is lost and it becomes amorphous; rehydration with water vapour then forms the pentahydrate rather than kernite.[561]

DISODIUM TETRABORATE MONOHYDRATE, $Na_2B_4O_7,H_2O$ OR $Na_2O,2B_2O_3,H_2O$

The 1:2:1 compound appears as a solid phase in the Na_2O–B_2O_3–H_2O system under pressure from about 115° to above 195°C[1058], and in the $Na_2B_4O_7$–H_2O system from 161° to 260°C.[1203] The principal lines in the *X*-ray diffraction pattern of the 1:2:1 compound have been reported.[1058] The monohydrate crystallizes from a suitable mixture of $Na_2B_4O_7,5H_2O$ and $NaBO_2,4H_2O$ at 150°C[974, 1058] or from borax solution above 177°C[975], and has been reported to crystallize from a solution containing more than 90% of $Na_2B_4O_7$ at 350°C, under pressure.[1203] A heat effect at 380°C in the thermal analysis of this crystallized material, under pressure, was interpreted as the decomposition of the 1:2:1 compound to give the anhydrous salt and a solution containing 10% of $Na_2B_4O_7$.[1203]

An amorphous material of the composition $Na_2B_4O_7,H_2O$ prepared by dehydration of borax, dissolves in methanol at 130°C in 2 h under various pressures of carbon dioxide as follows: 3·5 molecules of boron per litre at 3 atm of carbon dioxide, 3·9 molecules at 5 atm, and 4·0 molecules at 10 atm.[1152]

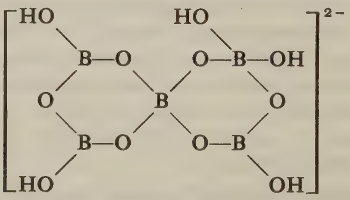

FIG. 7.—Divalent pentaborate ion postulated for ezcurrite[160, 230]

Tetrasodium Decaborate Hydrates

EZCURRITE, SUHR'S SODIUM BORATE, $Na_4B_{10\cdot2}O_{17\cdot5},7H_2O$ OR $2Na_2O,5{\cdot}1B_2O_3,7H_2O$

The 2:5·1:7 compound, triclinic, *d* 2·053, is a stable phase in the Na_2O–B_2O_3–H_2O system at temperatures from below 40° to above 94°C.[619] A mineralogical study has been made[346] and *X*-ray diffraction patterns have been reported.[168, 346, 588, 1114A] The infra-red spectrum has been studied.[898] It has been postulated[160, 230] that this compound contains discrete pentaborate ions having a 'triangular' boron atom replaced by a tetrahedral boron atom. This structure, Fig. 7, would be represented by the formula $Na_2^+[B_5O_6(OH)_5]^{2-}$. A recent crystal structure determination[138A] indicates that in ezcurrite the two-ring units shown in Fig. 7 are polymerized to form chains. These may be considered as formed by the elimination of a water molecule between one of the OH groups on the non-central tetrahedral boron atom and one of the OH groups on the other ring of the next unit. The structural formula then becomes $Na_2[B_5O_7(OH)_3],2H_2O$.

The composition of ezcurrite was first thought to be $3Na_2O,8B_2O_3,10H_2O$[957], but at present it is usually regarded as $2Na_2O,5B_2O_3,7H_2O$. However, analyses of various natural and synthetic samples have given $Na_2O:B_2O_3$ molar ratios appreciably less than the theoretical value of 0·4.[168, 346, 588, 619, 619A] Molar ratios as low as 0·376 have been reported[346] for the naturally occurring mineral. Experiments have indicated that the molar ratio of synthetic material is between 0·39 and 0·395; analysis of typical crystals gave 0·392 for the molar ratio, corresponding to $2Na_2O,$-$5{\cdot}1B_2O_3,7H_2O$.[619, 619A] The deficiency of Na_2O is, therefore, believed to be real. No satisfactory explanation has been proposed.

According to the solubility isotherms, a saturated solution of the 2:5·1:7 compound contains 11·5% of B_2O_3 at 60°, 13·6% at 75°, and 16·9% at 94°C.[619, 619A] This solubility curve crosses that of Auger's borate ($2Na_2O,5B_2O_3,5H_2O$) at about 90°C, indicating that the transition point from Suhr's borate to Auger's is at that temperature. Another solubility study[569] gave different results, leading the authors to conclude that the Suhr's–Auger's transition point is at 135°C; this study included a 100°C isotherm for the Na_2O–B_2O_3–H_2O system and a diagram showing the stability field of Suhr's borate in the ternary system below 100°C.[569] Parts of these curves evidently represent solutions supersaturated with respect to Auger's borate, which has been shown to be stable at temperatures as low as 87°C.[619, 619A] From a study of solubilities and heating curves under pressure, a composition–temperature diagram for the system $2Na_2O,5B_2O_3$–H_2O was constructed[569]; this indicated that in contact with solution, the trihydrate was formed at 195°C, the monohydrate at 240°C and the anhydrous salt at 335°C.

A solution saturated with both borax and Suhr's borate has a molar ratio ($Na_2O:B_2O_3$) equal to 0·295 at 40°, 0·364 at 50°, and 0·468 at 60°C[619, 619A], suggesting that Suhr's borate is stable in its own solution above about 54°C. Another solubility study has indicated this temperature limit to be 57°C.[569] The stability field of Suhr's borate extends down to 35°C.[569] The solubility is much lower and the stability region is much enlarged when sodium chloride is present.[957] Solutions supersaturated with Suhr's borate are easily formed.[569, 619] The elongated synthetic crystals, sometimes lath-shaped, are usually less than 0·1 mm in length.[619, 619A]

A DTA curve showed an endothermic peak at 260–265°C[588]; a restudy[346] showed endothermic peaks at 280° (loss of water), 575° (loss of OH), and 780°C (melting), and an exothermic peak at 680°C (crystallization). Thermogravimetric analysis showed water loss beginning at 160°C.[569] The curve did not indicate any lower stages of hydration. Five of the seven molecules of water were lost on heating at 270°C for 5 h; the last two were lost more slowly on heating to 500°C.

NASINITE, AUGER'S SODIUM BORATE, $Na_4B_{10}O_{17},5H_2O$ OR $2Na_2O,5B_2O_3,5H_2O$

The 2:5:5 compound, specific gravity 2·135 at 21°C[619], is stable in contact with its solution between 90°[619] and about 195°C.[569] An analysis has indicated a water content of seven molecules[167–8, 234], but this appears to have been due to an impure sample, because the original analysis[36] and later analyses[569, 619, 619A] agreed that the water content was five molecules.

It has been postulated[230] that the borate ion in Auger's sodium borate is $[B_5O_6(OH)_5]^{2-}$, the same anion as that postulated for ezcurrite, (Fig. 7), but the dehydration and hydration behaviour suggest a structure like that of Auger's potassium borate (p. 392). *X*-Ray patterns[167, 168, 569, 1114A], the infra-red absorption spectrum[898], and the optical properties of an apparently impure sample containing seven molecules of water[167, 168, 234], have been reported.

Saturated solutions of Auger's sodium borate in water contain 15·6% of B_2O_3 at 75° and 16·2% at 94°C.[619, 619A] The solubility curve crosses that of Suhr's borate at about 90°C, indicating that this temperature is the transition point of Suhr's borate to Auger's borate. Another study[569] gave different solubility values and a transition point of 135°C, which is believed to be incorrect. According to thermal analysis studies[569], Auger's sodium borate decomposes at 195°C, under pressure in contact with its saturated solution (38·5% $2Na_2O,5B_2O_3$) to form the trihydrate.

Auger's borate crystallizes slowly, and solutions supersaturated with it are easily prepared.[619, 619A] The slow crystallization would explain Auger's observation[36] that borax pentahydrate can crystallize from an Auger's borate solution in the presence of Auger's borate crystals. The somewhat elongated synthetic crystals are usually 0·2 mm or less in length and tend to form aggregates.[619]

A thermogravimetric curve of Auger's sodium borate[569] showed breaks at about 165°C at the composition, $2Na_2O,5B_2O_3,3H_2O$ and at the monohydrate composition at about 310–390°C. If the heating is stopped at about 300°C before the decomposition of $2Na_2O,5B_2O_3,H_2O$, the product can be rehydrated in air at 100% humidity to form the trihydrate and pentahydrate again. If the heating is continued to form the anhydrous salt at about 500°C, rehydration to form the trihydrate and pentahydrate does not occur.[569]

A differential thermal curve on a sample of Auger's sodium borate (which was evidently impure as it contained seven molecules of water) showed endothermal peaks at 70° and 130°C, two broad endothermal peaks at 190° and 330°C, and a sharp endothermal peak at 400°C.[167, 168, 234] Heating this sample in an oven resulted in a loss of 3·2 of the seven molecules of water below 110°C.[168]

BIRINGUCCITE, TETRASODIUM DECABORATE TRIHYDRATE, $2Na_2O,5B_2O_3,3H_2O$ OR $Na_4B_{10}O_{17},3H_2O$

Formation of crystals believed to be the 2:5:4 compound has been reported from borax–boric acid mixtures having $Na_2O:B_2O_3$ molar ratios 1:2 to 1:5, at 150–250°C in an autoclave; analysis gave 3·82 molecules of water.[167, 234] The *X*-ray diffraction pattern[167] shows some similarity to that of the trihydrate[569], and a more recent structure determination has shown that the composition is actually $2Na_2O,B_{10}O_{16}(OH)_2,2H_2O$. The density is 2·32 (observed), 2·297 (calculated). The structure is composed of the basic unit $[B_{10}O_{16}(OH)_2]^{4-}$ polymerized into sheets. The platy habit and perfect (001) cleavage are consistent with the sheet structure.[1254] Optical properties have been determined.[167] Differential thermal curve[167, 168, 234] shows endothermic peaks at 70°, 130°, 400°, and 470°C, an exothermic peak at about 570°C, and probable melting at about 650°C. When the compound was heated in an oven for 10 h at increasing temperatures, no evidence was observed of the formation of lower hydrates. The water content after heating at temperatures up to 110°C was about 0·8 molecule.[168] The *X*-ray diffraction pattern of heated biringuccite indicates that it is partly changed to another phase at 410°C. At 490°C, both phases disappear with formation of another phase which persists at 540°C.[167]

As mentioned above in the discussion of Auger's borate, formation of the 2:5:3 compound has been reported in the $2Na_2O,5B_2O_3–H_2O$ system under pressure between 195° and 240°C[569], with the solubility varying from 38·5% of $2Na_2O,5B_2O_3$ at 195° to 54·5% at 240°C.[569] It was also formed at 160°C in a thermogravimetric study of the pentahydrate; it can be dehydrated to the monohydrate, and in humid air, formed again from the monohydrate.[569]

TETRASODIUM DECABORATE MONOHYDRATE, $Na_4B_{10}O_{17},H_2O$ OR $2Na_2O,5B_2O_3,H_2O$

Formation of the 2:5:1 compound has been reported in the $2Na_2O,5B_2O_3$–H_2O system under pressure between 240° and 335°C.[569] Its *X*-ray diffraction pattern has been published.[569] The solubility decreases from 54·5% of anhydrous salt at 240° to 37% at 335°C. At 335°C in contact with its solution, it decomposes to form the anhydrous salt.[569] It is also formed during thermogravimetric analysis at about 310°C and can be rehydrated in humid air to form the trihydrate and pentahydrate.[569]

Sodium Triborate Hydrates

SODIUM TRIBORATE DIHYDRATE, $NaB_3O_5,2H_2O$ OR $Na_2O,3B_2O_3,4H_2O$

Two 1:3:4 compounds have been reported. The *X*-ray diffraction pattern of a synthetic 1:3:4 compound[421A, 471A] was different from that of ameghinite[33], a mineral of about the same composition found in Argentina. The synthetic material crystallized when a small amount of sodium metaborate (dried to the $NaBO_2,2H_2O$ composition) was added to a slurry of the 2:9:11 compound at 100°C.[471A] Its isotherm, between those of the 2:5:7 and 2:9:11 compounds, is very short at 100°C but longer at 130°C.[421A, 471A]

Ameghinite, specific gravity 2·03, also has the $Na_2O,3B_2O_3,4H_2O$ composition, as indicated by its specific gravity and its unit-cell volume, although analysis of an impure specimen corresponded to $4Na_2O,11B_2O_3,15H_2O$.[33] Its indexed *X*-ray diffraction pattern has been reported.[33] Its differential thermal curve has endothermic peaks at 245° and 780°C and an exothermic peak at 635°C.[33] Its occurrence, morphology, and physical and optical properties have been described.[33]

Disodium Enneaborate Undecahydrate, Sodium (2:9) Borate 11-Hydrate, $Na_4B_{18}O_{29},11H_2O$ or $2Na_2O,9B_2O_3,11H_2O$

If nuclei are present, the 2:9:11 compound, specific gravity 1·903[619], crystallizes slowly from saturated sodium pentaborate solutions at temperatures near the boiling point. Its *X*-ray diffraction pattern has been published.[1114A] Solutions supersaturated with it are easily formed.[619, 619A] Its saturated solutions contain 21·6% of B_2O_3 at 50°; 23·4% at 60°; 26·7% at 75°; and 31·2% at 94°C. In the solutions (molar ratio $Na_2O,B_2O_3 = 0{\cdot}222$), the solubility curve for sodium pentaborate crosses that for the (2:9) borate at 57°C, indicating that sodium (2:9) borate is stable in contact with its own solution above that temperature.[619, 619A] Its 50°, 60°, 75° and 94°C[619], and its 64°, 80° and 100°C[421A, 471A] isotherms have been determined.

Sodium Pentaborate Hydrates

SOLUBILITY

Sodium pentaborate pentahydrate is stable in contact with its own solutions between 2° and 59·5°C[619, 619A], borax being the stable phase below 2°C and sodium (2:9) borate 11-hydrate being the stable phase above 59·5°C. However, supersaturation with these stable phases occurs so easily that there is no experimental difficulty in obtaining a solubility curve, with the 1:5:10 compound as the solid phase, from the cryohydric point to the boiling point. Solubilities (Fig. 4) at atmospheric pressure have been studied in several laboratories.[93, 619, 619A, 699, 700] The values considered most reliable[619] are listed in Table IX. When seeded with the 1:5:4 compound, the solubility is 50·2% at 98°C and 55·6% at 107°C, indicating that a metastable transition point to the 1:5:4 compound exists between these temperatures.[619, 619A] The most recent solubility values at higher temperatures, under pressure, are listed in Table X. The earlier[105] and more recent work[1201A] differ in the solid phases reported to exist between 225° and 256°C.

When a saturated sodium pentaborate solution is agitated for some time at temperatures near its boiling point, the compound $2Na_2O,9B_2O_3,11H_2O$ will crystal-

Table IX.—Solubility of $NaB_5O_8,5H_2O$ *in Water*

(Expressed as wt-% of NaB_5O_8. The solid phase throughout is $NaB_5O_8,5H_2O$, −1·7°C being the cryohydric point)

Temperature, °C	Solubility	Temperature, °C	Solubility
−1·7	5·5	55	24·30
0	5·77	60	26·88
5	6·75	65	29·35
10	7·5	70	34·98
15	9·30	80	38·1
20	10·55	85	41·1
25	12·20	90	44·3
30	13·72	95	47·6
35	15·60	98	49·9
40	17·50	100	51·0
45	19·63	105	54·7
50	21·72	107	56·3

Table X.—Solubility of $NaB_5O_8,5H_2O$ *and Related Phases in Water at Increased Pressure*[1201A]

Temperature, °C	Solubility (wt-% NaB_5O_8)	Solid phases
106	55	1:5:10 and 1:5:4
117	63	1:5:10 and 1:5:2
225	71	1:5:4 and 1:5:2
256	76	1:5:4 and 1:5:1
308	79	1:5:2 and 1:5:1
350	82	1:5:1 and 1:5:0

lize very slowly if seed is present.[619, 619A] Several solubility[1201, 105] and heating-curve[1201A, 105, 107–8] studies have been made at temperatures above 100°C under pressure. The most recent study, made with a new apparatus, indicates that, in the absence of 2:9:11 seed, the 1:5:10 compound is in equilibrium with its solution up to 106°C, the 1:5:4 compound from 106° to 225°C, the 1:5:2 compound from 225° to 308°C, the 1:5:1 compound from 308° to 350°C and the anhydrous salt above 350°C.[1201A] The 1:5:10 compound may persist in a metastable state above 106°C without forming the stable 1:5:4 compound, but in this case it changes to the 1:5:2 compound at 117°C. Similarly the 1:5:4 compound may persist in the metastable state above 225°C, changing to the 1:5:1 compound at 256°C.[1201A] Differential thermal analysis, under pressure, using samples obtained by the rapid partial dehydration of the 1:5:10 compound, gave plateaux at 117°, 308° and 350°C, corresponding to the 1:5:2, 1:5:1 and 1:5:0 compounds.[1201A] Samples obtained by heating the 1:5:10 compound in a sealed tube at 150°C, or by heating to 100°C for one or two days, gave plateaux at 106°, 256° and 350°C, corresponding to the formation of the 1:5:4, 1:5:1 and 1:5:0 compounds.[1201A] A revised phase

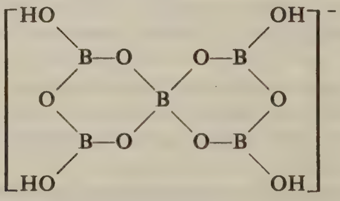

FIG. 8.—Univalent pentaborate ion in potassium pentaborate tetrahydrate[933]

diagram of the NaB_5O_8–H_2O system from 100° to 380°C, in the absence of seeds of the 2:9:11 compound, has been published.[1201A] Heating the 1:5:10 compound in a sealed vessel at 160°C for one to three days gave the 1:5:4 compound.[619, 619A] Heating under these conditions for a longer time or at lower temperatures (134° and 148°C) gave a mixture of 1:5:4 and 2:9:11. At 126°C in three days, in a sealed tube, the 2:9:11 compound was formed but not the 1:5:4 compound.[619, 619A]

SODIUM PENTABORATE PENTAHYDRATE, SBORGITE, $NaB_5O_8,5H_2O$ OR $Na_2O,5B_2O_3,10H_2O$

The 1:5:10 compound, triclinic, *d* 1·713[165], occurs at Larderello, Italy.[165] Its *X*-ray diffraction pattern[107, 165] has been published. Its structure has not been reported, but it probably contains the $[B_5O_6(OH)_4]^-$ ion also found in potassium pentaborate pentahydrate[930, 933], consisting of two perpendicular six-membered B–O rings sharing a tetrahedral boron atom (Fig. 8). Its infra-red spectrum has been published.[898] The electrical conductivity, during heating, showed a small peak at 130°C and a large increase between 520° and 760°C.[812] The specific magnetic susceptibility values for the pentahydrate and phases obtained by dehydration to 2, 1, 0·5 and 0 molecules of water content have been measured as $-0{\cdot}528$, $-0{\cdot}473$, $-0{\cdot}440$, $-0{\cdot}418$, and $-0{\cdot}390 \times 10^{-6}$ c.g.s. units, respectively.[663] The heat capacity of the pentahydrate has been determined from 15 to 345 K and the heat content, entropy, and other thermal functions have been tabulated from 0 to 345 K.[266]

The rate of dissolution of sodium pentaborate pentahydrate, studied by the revolving disk method, was lower than that predicted by theory for diffusive dissolution, indicating a mixed kinetic and diffusive process.[679] The etch figures correspond to the theoretical liquid flow lines.

Dehydration

When the 1:5:10 compound is dehydrated at room temperature over concentrated sulphuric acid, two molecules of water are lost in about a year.[559] When heated *in vacuo*, it is stable up to 75°C, where eight of the ten molecules of water are lost; the remaining two molecules are lost slowly as the temperature is increased to 350°C.[307] When the granular 1:5:10 compound was heated for one or two days at 129–180°C in an oven, a product of the approximate composition 1:5:4 having a distinct *X*-ray pattern[1114A] was produced.[619] When the 1:5:10 compound was heated for 24 h at 240°C in an oven, a product of the approximate composition 1:5:2 was formed[619], with an *X*-ray diffraction pattern[1114A] different from that of the 1:5:4 compound.

A thermogravimetric curve[166] of the 1:5:10 compound gave a slight inflection at 100° corresponding to the loss of two molecules of water, but other curves[1201A, 812] gave no inflection. A sample which had been heated in a sealed tube at 100°C, however, gave plateaux corresponding to the 1:5:4, 1:5:2, and 1:5:1 compounds.[1201A] A differential thermal curve showed endothermic effects beginning at 90°[812] or 100°C[166] with peaks at 150°[812] or 170°C.[166] There were also smaller exothermic peaks at 580° and 660°C and an endothermic peak at 750°C.[812]

Chemical Reactions

Sodium pentaborate reacts with methanol to give trimethyl borate (methanol azeotrope) in good yield.[1149] The composition $NaB_5O_8,6H_2O$ is readily soluble in methanol.[166] The Fischer titration of sodium pentaborate corresponds to 12·8 molecules of water, compared with the expected twelve.[166] When a pentaborate is heated with an alkylene glycol until at least one molecule of water has been removed per atom of boron, a condensate is formed which is a corrosion inhibitor for hydraulic fluids.[1187]

SODIUM PENTABORATE DIHYDRATE, $NaB_5O_8,2H_2O$ OR $Na_2O,5B_2O_3,4H_2O$

The 1:5:4 compound, produced by dehydration of the 1:5:10 compound in an oven at 129–180°C[619] has an *X*-ray pattern[1114A] similar to that[107] of a hydrate regarded by previous investigators as the 1:5:2 compound.[105, 108] No analysis was published for this latter product. Recent work indicates that the 1:5:4 compound is in equilibrium with its solution, under pressure, between 106° and 225°C, changing to the 1:5:2 compound at 225°C.[1201A] It may, however, remain in the metastable state up to 256°C, changing to the 1:5:1 compound at that temperature.[1201A]

SODIUM PENTABORATE MONOHYDRATE, NaB_5O_8,H_2O OR $Na_2O,5B_2O_3,2H_2O$

The 1:5:2 compound, produced by dehydration of the 1:5:10 compound in an oven at 240°C, has an *X*-ray pattern different from that of the hydrate regarded by previous investigators as the 1:5:2 compound.[105, 107–8] It is in equilibrium with its solution between 225° and 308°C, but may appear at 117°C when a rapidly but incompletely dehydrated pentahydrate is heated under pressure.[1201A]

SODIUM PENTABORATE HEMIHYDRATE, $NaB_5O_8,0{\cdot}5H_2O$ OR $Na_2O,5B_2O_3,H_2O$

The 1:5:1 compound was reported, from solubility and heating curve studies under pressure, to be in equilibrium with its solutions between 308° and 350°C, decomposing at 350°C to form the anhydrous salt.[1201A]

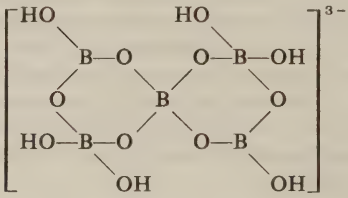

FIG. 9.—Trivalent pentaborate ion in ulexite[170, 171, 173]

Hydrated Double Salts of Sodium Borates

ULEXITE, $Na_2O,2CaO,5B_2O_3,16H_2O$

Ulexite is triclinic, *d* 1·955. The structure[170–1, 173], previously predicted[160], is represented by the formula $NaCaB_5O_6(OH)_6,5H_2O$. It contains the discrete polyion $[B_5O_6(OH)_6]^{3-}$, which is the two-ring pentaborate ion in which two opposite boron atoms are made tetrahedral by the addition of a hydroxyl group to each (Fig. 9); n.m.r. studies are in agreement with this structure.[472] The infra-red spectrum[819, 880, 898], and indexed *X*-ray diffraction patterns[166, 173] have been reported.

When ulexite was heated gradually, dehydration began at about 60°C and was complete at 500°C.[1176] Heating for 12-h periods at temperatures increasing by 30° intervals gave a gravimetric curve with an inflection at 70–90°C corresponding to a loss of four molecules of water. *X*-Ray diffraction showed that a new phase, $Na_2O,2CaO,5B_2O_3,12H_2O$ was present.[166] Loss of the next eight molecules was rapid between 100° and 120°C, and the last four were lost slowly between 120° and 400°C.[166] In another study twelve molecules were lost between 103° and 180°C, and the last four between 270° and 500°C.[383]

A published DTA curve has an exothermic peak at 190–200°C.[11, 166] Other investigations showed endothermic effects at 110–310°C (167·3 kcal mole^{-1}) and 370–520° (133·5 kcal mole^{-1})[1176]; at 135°, 163°, and 191°C[325]; and at 145° and 180°C.[383] There was an exothermic effect at 520–600°C.[1176] Dehydration results at constant temperatures were interpreted as indicating a series of hydrates.[851A]

Some specimens of ulexite have the interesting optical property that if an object is held against one surface of a section cut perpendicular to the parallel fibres, an image of the object is projected to the opposite surface owing to reflections along the fibre interfaces.[60A, 896]

A colloidal form of ulexite, made by suspending a mixture of four molecules of borax and two molecules of lime in water, is said to have advantages over borax as a ceramic raw material.[312A]

Chemical Reactions

When an excess of ulexite is agitated with water at 25°C, the resulting sodium concentration corresponds to 0·49% of $NaCaB_5O_9$.[847] Calcining ulexite at 200–500°C increases its solubility to 9–13 g l^{-1}.[1240]

A study of the dissolving of ulexite in acids indicates that the rate of dissolution decreases at higher nitric acid concentrations.[352] In hydrochloric acid, increasing the acid concentration decreases the rate of dissolution at 25°C to a constant value.[940] This behaviour is attributed to formation of a boric acid film. In other studies of the decomposition rate in 0–40% hydrochloric acid at 25°C, and in 0–100% sulphuric acid at 25–100°C, maxima were also observed on the plot of rate of dissolution against acid concentration.[941–3]

Ulexite reacts with concentrated ferric or aluminium sulphate solution to precipitate ferric or aluminium hydroxide and calcium sulphate. After filtration, sodium pentaborate crystallizes when the solution is cooled.[1011] Ulexite reacts with a slight excess of a mixture of sodium carbonate and sodium hydroxide to give a sodium metaborate solution.[1038]

With the Fischer reagent, ulexite reacts very slowly, giving an apparent 15·9 molecules of water rather than the theoretical 17.[166]

PROBERTITE, $Na_2O,2CaO,5B_2O_3,10H_2O$

Probertite, monoclinic, contains the polyions of ulexite, polymerized by elimination of water to form $[B_5O_7(OH)_4]_n^{3n-}$ chains.[171, 173, 465, 715]

An indexed powder diffraction pattern[173], unit-cell and space-group data[54], and the infra-red absorption spectrum[819, 880, 898] have been published.[173]

The DTA curve has endothermic peaks at 140°, 250°, and 260°C[11] or, in other work, 170°, 250°, and 270°C.[166] A thermogravimetric curve (12 h heating at various temperatures)[166] has a horizontal portion at about 100°C corresponding to the loss of two of the ten molecules of water. There is a loss of four molecules during heating from 100° and 180°C and a slower loss of the last four molecules between 180° and 400°C.[166]

Heating probertite at 100°C gave an unchanged probertite *X*-ray diffraction pattern; heating at 190°C gave an analogous but weaker pattern; and heating at 410°C gave only broad bands.[166]

SODIUM STRONTIUM PENTABORATE OCTAHYDRATE, $NaSrB_5O_9,8H_2O$ OR $Na_2O,2SrO,5B_2O_3,16H_2O$

Sodium strontium pentaborate, *d* 2·06, may be crystallized from a solution of strontium chloride, borax and sodium hydroxide. Its solubility is 7·4 g l^{-1} of solution at 20°C. The octahydrate loses one molecule of water at 64°C, five more at 64–120°C, one more at 150–190°C, and the last molecule at 250–320°C. Its differential thermal curve has been published.[805]

TEEPLEITE, $NaBO_2,NaCl,2H_2O$

Teepleite, tetragonal, *d* 2·076[257], is synthesized from aqueous solutions of sodium metaborate and sodium chloride. Its unit-cell data and its indexed *X*-ray diffraction pattern have been determined.[710] The structure contains tetrahedral $B(OH)_4^-$ groups[257], as shown by infra-red and nuclear quadrupole resonance studies[710]; it contains no H_2O molecules.[258] When calcined, teepleite decomposes to form a mixture of sodium chloride and sodium metaborate.[257] Its infra-red[413, 898] and Raman spectra[413] have been reported.

RIVADAVITE, $3Na_2O,MgO,12B_2O_3,22H_2O$

Rivadavite, monoclinic, *d* 1·905, found in a borax deposit in Argentina, has been described crystallographically and studied by *X*-rays and DTA.[345]

ANHYDROUS SODIUM BORATES

Phase Equilibria in the System Na_2O–B_2O_3

A study of the Na_2O–B_2O_3 system[581] using the preferred quenching method as far as possible gave liquidus curves for the compounds with $Na_2O:B_2O_3$ molar ratios 1:1, 1:2, 1:3, and 1:4 in the region from $Na_2O:B_2O_3$ to B_2O_3, and showed the existence of the 2:1 compound. Another study[366], by means of heating curves, gave melting points and *X*-ray diffraction data on the stable and low-melting forms of the 1:4, 1:3 and 1:2 compounds. There was also a previous study of crystallization in this system, using a temperature-gradient furnace.[653] A more recent heating-curve study of samples devitrified by heat treatment at various temperatures showed the existence of the 3:1, 5:2, 3:2, 2:3, 2:5, 1:5, and 1:9 compounds.[570] Compounds having the compositions 2:3 and 4:5[869,871,874] and 4:7[872,875] have been reported but the 4:5 and 4:7 compounds have not been observed in later work.[570] The eutectics in this system have been determined and are listed in Table XI.

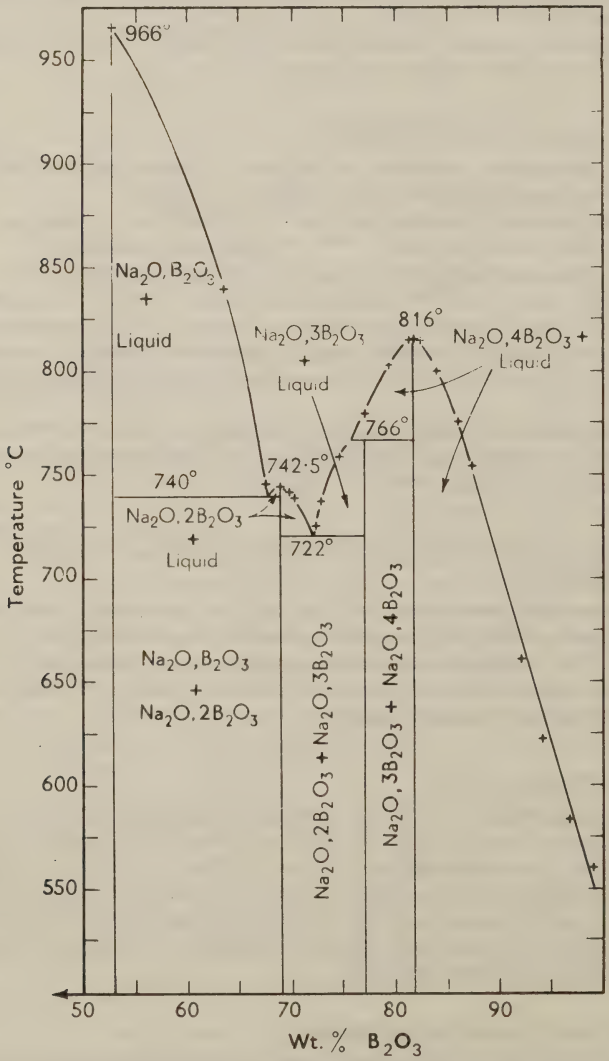

FIG. 10.—Phase equilibrium relations for the usual compounds in the binary system Na_2O-B_2O_3[581]

Table XI.—Eutectics in the Na_2O–B_2O_3 *System*

$Na_2O:B_2O_3$ ratios in compounds present	Melting temperature, °C	Wt-% of Na_2O
γ-Na_2O–3:1	455°[570]	79·8[570]
3:1–2:1	570°[570], 535°[958]	67·4[570], 66·5[958]
2:1–1:1	632°[570], 610°[958]	62·5[570], 62[958]
1:1–1:2	740°[581]	32[581], 31[570]
1:2–1:3	722°[581], 728°[570]	27·7[581], 26·9[570]
		Mole-% of B_2O_3
β-1:2–1:3 (metastable)	640°[570]	68
β-1:1–1:3 (metastable)	640°[570]	67·8
1:2–1:4 (metastable)	725°[570]	71·5

The free energies of formation of the 1:1, 1:2, 1:3 and 1:4 compounds from Na_2O and B_2O_3 have been plotted against the composition to show the regions of stability of the compounds.[839] The heat of crystallization per oxygen atom has been determined at 10, 20, 25 and 33·3 mole-% of Na_2O, from 25° to 700°C.[783]

Crystalline Anhydrous Sodium Borates

TRISODIUM MONOBORATE, SODIUM ORTHOBORATE, Na_3BO_3 OR $3Na_2O,B_2O_3$

Physical Properties

The 3:1 compound, m.p. 675°C, has been prepared from the oxides, and its *X*-ray diffraction pattern has been reported.[570] A study of the force constants of the BO_3^{3-} ion has been made[763], and the infra-red absorption spectrum has been studied.[636A]

Chemical Reactions

The reaction of stoichiometric amounts of boric acid with sodium carbonate to give sodium orthoborate has been studied by thermogravimetry, differential thermal analysis and infra-red spectrography.[636A] The existence of Na_3BO_3 has been supported by experiments in which boric oxide was melted with an excess of sodium hydroxide, resulting in a loss of three molecules of water per molecule of boric oxide (ref. [1083], No. 21, p. 650). The reaction of boric oxide with excess of sodium carbonate has been interpreted to indicate that the 3:1 and 1:1 compounds are also formed above 350–390°C.[148]

The 3:1 compound has been found to stabilize the high-temperature form of dicalcium silicate, Ca_2SiO_4[265] and to catalyze the esterification of end OH-groups of polyformaldehyde by anhydrides or ketene.[1018] Heated with ferric oxide at 1200°C in air for 18 h, it forms a mixture of green $FeBO_3$ and black Fe_3BO_6 crystals.[920]

DECASODIUM TETRABORATE, $Na_{10}B_4O_{11}$ OR $5Na_2O,2B_2O_3$

The 5:2 compound has been prepared from the oxides by heating for 5 days at 380°C, and its *X*-ray diffraction pattern has been published.[570] Graphical methods appear to lead to the 5:2 formula, although a composition such as 7:3 may be possible.[570] Its DTA curve shows a marked thermal effect at 520°C which has been attributed to a peritectoid decomposition to form the 3:1 and 1:1 compounds.[570]

TETRASODIUM DIBORATE, $Na_4B_2O_5$ OR $2Na_2O,B_2O_3$

The 2:1 compound, congruent m.p. 640°[570], or 625°[581], or 620°C[958], has been prepared from the oxides[570] or from borax and sodium hydroxide or carbonate.[581] Its *X*-ray diffraction pattern[471A, 570] has been reported, and its infra-red absorption spectrum determined.[899] It crystallizes very readily but in small quantities it can be obtained as a glass.[581] Its optical properties have been reported.[581]

HEXASODIUM TETRABORATE, $Na_6B_4O_9$ OR $3Na_2O,2B_2O_3$

The 3:2 compound has been prepared by heating an Na_2O–B_2O_3 mixture containing 50 to 73 wt-% of Na_2O at about 500°C. Its *X*-ray pattern could not be obtained, possibly because of a low-temperature eutectoid reaction.[570] It undergoes a solid-state decomposition at 575°C[570], giving the 2:1 and β-1:1 compounds.[570]

α-SODIUM METABORATE, $NaBO_2$ OR Na_2O,B_2O_3

Physical Properties

The α-form of the 1:1 compound, rhombohedral, m.p. 966°[581], or 968°C[570], specific gravity 2·464, is easily made by dehydration of the 1:1:8 compound.[570] The water content is about 1·3% after heating for four days at 170°C *in vacuo*, but the product becomes almost water-free at 500°C.[560]

Its *X*-ray pattern has been reported.[107,177,1114A] The structure[243–4,530] consists of planar $B_3O_6^{3-}$ rings composed of three BO_3 triangles with two of the three corners shared. There is a large difference in the B–O bond-lengths.[530] The structure has been discussed in terms of the 'structon' theory.[1247] The melting points of sodium, potassium and lithium metaborates have been represented by an empirical equation involving the polarizability and radius of the ions.[264]

The optical properties have been determined.[581] The infra-red absorption spectrum is somewhat similar to that of potassium metaborate[315,899]; these two compounds are isomorphous. In one study, infra-red spectra of old and of freshly prepared samples were found to be quite different[224–5]; the changes were attributed to the formation of polymeric groups, but hydration, which occurred[315] in another study[568], appears to be a more likely cause. Infra-red studies on the metaborate have indicated that the BO_2^- ion is not monomeric[223]; other infra-red studies of the BO_2^- ion have been reported.[910] The ^{11}B n.m.r. spectrum has been compared with computer-simulated spectra.[60]

Molten sodium metaborate can be supercooled to only 122° below its melting point.[883] Amorphous sodium metaborate has not been reported, although dehydration has been carried out at as low a temperature as possible *in vacuo*.[560] The specific magnetic susceptibility of sodium metaborate dehydrated by heating above 200°C is $-0{\cdot}477 \times 10^{-6}$ c.g.s. units.[663]

Thermochemical Data

From the freezing-point diagrams and other studies of the $NaBO_2$–NaF system, the heat of fusion of sodium metaborate was determined to be 8000 g cal $mole^{-1}$.[649] The U.S. National Bureau of Standards, in 1952, evaluated the heat of formation of the crystalline metaborate at 25°C as −253 kcal $mole^{-1}$.[1118] Later, the values −234·3[1147], −235·9[292], and −233·2[2] (−31·5 from the oxides) were calculated from the heats of solution in nitric and hydrochloric acids, respectively. The standard free-energy of formation at 25°C was calculated to be −219·8 kcal $mole^{-1}$ (−31·2 from the oxides).[2] The heat capacity, entropy, free-energy function, heat content, and heat and free energy of formation, based on estimates where necessary, have been tabulated for crystalline sodium metaborate from 0 to 2000 K and for the gaseous metaborate from 0 to 6000 K.[291,1085,1124] A subsequent tabulation, based on experimental enthalpies, provided somewhat different values of these quantities at temperatures up to the melting point.[1016] Heat capacity and other thermodynamic functions at 6–350 K have been tabulated[291] and extrapolations to 1000 K have been attempted.[1124] The heat capacity at 25°C is 15·76 g cal $mole^{-1}$ °C.[291]

β-SODIUM METABORATE, $NaBO_2$ OR Na_2O,B_2O_3

The β form is metastable and obtained with difficulty. Its *X*-ray diffraction pattern, determined on a sample fused and quenched in air and then reheated to about

700°C, has been published.[570] At 730°C, there is a transformation to the α-form; the metastable melting-point is 734°C.[570]

Chemical Reactions

Anhydrous sodium metaborate is hygroscopic, but less so than a product dehydrated to the $NaBO_2,H_2O$ composition over phosphorus pentoxide at room temperature.[559] The reaction of sodium metaborate with sodium hydroxide has been studied by chemical analysis and DTA up to 600°C. The amount of liberated water indicated that sodium orthoborate, Na_3BO_3, was formed.[567] The reaction started at 240–280°C, near the temperature at which sodium hydroxide undergoes a phase change. The amount of liberated water increased at 330–370°C, near the peritectic temperature in the $NaOH$–$NaBO_2$ phase diagram.[567] A mixture of sodium metaborate and elemental boron, heated *in vacuo* to 880–1800°C, forms BO vapour, which can be condensed at temperatures below 700°C to form polymeric BO.[1025]

Sodium metaborate stabilizes the high-temperature form of dicalcium silicate, Ca_2SiO_4.[265] Anhydrous sodium metaborate, dissolved in methanol, reacts with carbon monoxide under pressure to give sodium formate and a methanol solution of more acidic sodium borates, which can be distilled to give a trimethyl borate–methanol azeotrope.[983]

Other chemical reactions of sodium metaborate are given on pp. 456–72.

TETRASODIUM HEXABORATE, $Na_4B_6O_{11}$ OR $2Na_2O,3B_2O_3$

The 2:3 compound, formed at 490°C from sodium metaborate and disodium tetraborate, decomposes at 720°C to form β-$Na_2O,2B_2O_3$ and α-$Na_2O,2B_2O_3$.[570, 872, 875] It also decomposes when cooled to give these same substances.[570] For this reason, its *X*-ray pattern has not been published. A compound having the provisional formula $2Na_2O,3B_2O_3$ appeared in a visual-polythermal study of phase equilibria in the $Na_2B_4O_7$–$NaBO_2$–Na_2CrO_4 system.[869] It melts incongruently.

OCTASODIUM DECABORATE, $Na_8B_{10}O_{19}$ OR $4Na_2O,5B_2O_3$

An incongruently melting compound having the provisional formula $4Na_2O,5B_2O_3$ appeared in certain visual polythermal studies of phase equilibria.[869, 874] A 4:7 compound was also reported in a system containing chromate[872, 875], but has not been found by other investigators.

DISODIUM TETRABORATE, ANHYDROUS BORAX, $Na_2B_4O_7$ OR $Na_2O,2B_2O_3$

The 1:2 compound exists in at least three crystalline forms. The usual α-form (or 'B-form'[564]), made by dehydration of borax hydrates, is the stable form above 600–700°C, and melts congruently at 742·5°C.[581] Melting points as low as 732°C, with errors attributed[581] to absorption of water from the atmosphere, have been published. 'Calcined borax', apparently partially dehydrated, has been recorded to melt at 685–716°C.[216] The α-form crystallizes when supercooled molten borax is seeded[564] or touched[198] at 600–680°C. The linear rate of crystallization has been investigated.[1246] Forms designated 'A' and 'C', m.p. 710°C and 663°C (incomplete melting) respectively, were at times obtained rather than the B-form, when the melt was kept at 600–680°C for 10 h or more without seeding.[564] Form A was unchanged after six weeks at 600–630°C. Experiments suggested that when form C melted, form A crystallized and when form A melted, form B crystallized.[564] In another investigation, two forms designated β and γ were obtained in addition to the α-form[581] and their optical properties were determined. The β-form changed into the α-form in 20 min at temperatures above 600°C. This change takes place at temperatures as low as 475°C, but it is slow at the lower temperatures.[581] The γ-form was unaltered in 15 min at 700°C, but changed partly to the α-form in 4 h at this temperature, and completely to the α-form in 15 min at 625°C.[581] Whether this β-form and the α-form[581] may have been form C and form A, respectively, of the previous work[564] is uncertain. *X*-Ray diffraction patterns of forms designated as β and γ have been published[570], but it is uncertain whether these are the same forms as β and γ, respectively, of the previous work.[581] A triclinic form has been reported[879], and crystal structure studies have been carried out on such a form.[1256]

α-DISODIUM TETRABORATE

Physical Properties and Thermochemical Data

The *X*-ray diffraction pattern[176,783], unit-cell dimensions, and probable space-group of an orthorhombic form, probably the α-form of the 1:2 compound have been given.[195–6] Thought first to have a cage structure[220], later crystal study shows a layer formation[1256] (d = 2·27, borax glass = 2·36). The optical properties have been determined.[176,581] The infra-red absorption spectrum has been studied[898]; peaks were observed[222] at 1069 (very broad), 1380, and 1470 cm^{-1}. Non-thermal (chemiluminescent) radiation has been observed from disodium tetraborate at temperatures as low as 700°K in an atmosphere of carbon monoxide containing nitrous oxide and oxygen. The temperature at which radiation occurs is 150–200°C less than with other salts investigated. The radiation was intense when the nitrous oxide concentration was 8 to 20%.[749] The specific magnetic susceptibility of borax dehydrated above 318°C was found to be $-0{\cdot}423\times10^{-6}$ c.g.s. units.[663]

The heat of formation of crystalline disodium tetraborate, $Na_2B_4O_7$, at 25°C has been calculated to be $-786{\cdot}4$ kcal mole^{-1} [292,1147], from its heat of solution in nitric acid.[750] A calculation based on heat of solution measurements in hydrochloric acid and a later value of the heat of formation of boric oxide also gave $-786{\cdot}4$ kcal mole^{-1}.[2] This value is preferable to the older value, $-777{\cdot}7$ kcal mole^{-1} [1118], which appears to be for the glassy form. The free energy of formation from the elements is $-739{\cdot}7$ kcal mole^{-1}.[2,904] The heat of devitrification is $-4{\cdot}99$[904] or $-4{\cdot}85$[750] kcal mole^{-1}. The standard free energy of devitrification is $-4{\cdot}81$ kcal mole^{-1}.[780] Heat capacity values measured by adiabatic calorimetry and values of S°, $(H^\circ-H^\circ_0)$ and $(F^\circ-H^\circ_0)/T$ have been tabulated from 6–350 K for the α-form and for the vitreous form.[904] The heat capacity of the α-form is higher than that of the vitreous form at temperatures above 35 K.[904,1120] Extrapolated heat capacity values for crystalline disodium tetraborate have been tabulated for temperatures of 400–1000 K.[1124] Experimental heat contents for crystalline anhydrous borax, from 25°C[1016] and from 100°C[780,783] to the melting point, and for the amorphous form from 25° to 1100°C have been reported.[780,783] The small difference between the entropies of the glassy and crystalline forms suggests a similarity in structure.[780] Heat capacity, entropy, free-energy function, enthalpy, and heat and free energy of formation have been calculated from literature values and tabulated from 0 to 2000 K for crystalline anhydrous borax and from 298 to 3000 K for liquid anhydrous borax.[1085] A later tabulation at temperatures up to the melting point was based on other experimental enthalpy values, and gave somewhat different values of these quantities.[1016] The heat capacity has been treated theoretically as the sum of contributions from the polymer chain anions and from the cation oscillators.[829]

The integral heat of solution of crystalline anhydrous borax in water to give a 2·5 wt-% $Na_2B_4O_7$ solution has been determined as $-46{\cdot}00$ g cal g^{-1} $Na_2B_4O_7$ at 51·5°C and $-45{\cdot}50$ g cal at 60°C.[737]

Chemical Properties

Crystalline anhydrous borax takes up some water from moist air even at 300°C. It becomes anhydrous at 700°C, but will take up a little moisture from moist air when melted, at a temperature just above the melting point of 742·5°C.[581]

Anhydrous borax glass dissolves in water more slowly than the hydrated forms. From its rate of solution in stirred and unstirred water, the interface temperature gradient was found to be about 3°C.[603]

In an attempt to measure the vapour pressure of aqueous solutions saturated with anhydrous borax under pressure at 374–600°C, equilibrium with crystals was apparently not reached, since very viscous solutions were obtained.[580] Crystalline anhydrous borax dissolves slowly in methanol and will reach a concentration of

13 wt-% at 25°C; finely divided anhydrous borax will reach 16·7%.[1117A] It will slowly dissolve in ethylene glycol at 25°C, to make very viscous solutions containing 15·5% of $Na_2B_4O_7$. If it is finely divided, a concentration of 30% $Na_2B_4O_7$ is reached.[1117A] In formamide its solubility at 25°C is 40·6 g l^{-1} of saturated solution.[180]

Anhydrous borax does not react with dry carbon dioxide, but is completely decomposed by it if methanol is present to volatilize the boric oxide as trimethyl borate (ref. 1083, No. 21, p. 658). Dissolved in methanol, it reacts with carbon monoxide to produce sodium formate and solutions of more acidic sodium borates in methanol, from which trimethyl borate can be recovered.[983] It is quantitatively converted into sodium fluoride by evaporation to dryness with formic acid, volatilization of the boron with methanol, and evaporation to dryness with hydrofluoric acid.[781] It is quantitatively converted to sodium fluoborate by evaporation to dryness with hydrofluoric acid.[581] Anhydrous borax, added to an aqueous solution containing hydrofluoric acid and potassium chloride precipitates potassium fluoborate. Gradual addition increases the particle size of the product.[1034] When heated to 100–200°C with a fluorosulfonate, it evolves boron trifluoride.[1200] Anhydrous borax reacts with sodium oxide at high temperatures to give anhydrous sodium metaborate or orthoborate, or a mixture, depending on conditions. The reaction can be started with a hot wire.[992–3] A mixture of anhydrous borax and sodium hydride, made by treating a mixture of sodium metal and anhydrous borax with hydrogen, reacts with coarse sea-sand and hydrogen at 450°C (4 h at 3–5 atm pressure) to give sodium borohydride.[982] Magnesium reduces anhydrous borax when a mixture of the two is heated. A fine, insoluble, brown powder is obtained when the reaction product is boiled with hydrochloric acid.[1117A] Molten borax attacks burnt clay at 800°C.[857] Anhydrous borax reacts with carbon and chlorine, at elevated temperatures, to give boron trichloride, sodium chloride and carbon monoxide. This process can be carried out in a high-intensity arc.[1168] Copper-containing materials are said to cause the reaction to proceed at lower temperatures, beginning at 400°C, giving very pure boron trichloride.[1003] Anhydrous borax is a weak or ineffective catalyst for the oxidation of sodium sulphite and various organic compounds.[585] Disodium tetraborate had a low chain-destroying efficiency in the hydrogen–oxygen reaction.[892] Borax glass is blackened by radium radiation filtered through mica.[474]

Other properties of liquid and glassy anhydrous borax are given in the section on the molten borates, pp. 437–72.

TETRASODIUM DECABORATE, $Na_4B_{10}O_{17}$ OR $2Na_2O,5B_2O_3$

A phase-equilibrium diagram[570] indicates that the 2:5 compound is stable between 580° and 686°C, a mixture of the α-1:2 and γ-1:3 borates being formed at higher and lower temperatures. The 2:5 compound can be obtained by heating the molten glass of this composition at about 500°C for two days. It crystallizes completely at 580°C[570] and can be obtained at room temperature by rapid cooling. Its *X*-ray diffraction pattern has been published.[570] A thermal effect shown by the heating curves in the system $2Na_2O,5B_2O_3–H_2O$ under pressure at about 500°C has been attributed to crystallization of the anhydrous 2:5 compound.[569]

SODIUM TRIBORATE, NaB_3O_5 OR $Na_2O,3B_2O_3$

The 1:3 compound exists in three forms.[570] The stable α-form, monoclinic, *d* (calculated) 2·242[1257] incongruent m.p. 766°C, decomposes at that temperature to give the 1:4 compound and a liquid containing 76% of B_2O_3[581] (or 74% of B_2O_3[570]). The *X*-ray diffraction pattern[135, 176, 570, 783, 903], optical properties[176, 581], and infra-red absorption spectrum[899] have been published, and the crystal structure has been studied.[1257] Arguments have been published for a cage structure.[220]

From measurements of its heat of solution in hydrochloric acid, the heat of formation of sodium triborate from its elements has been evaluated as $-549·9$ kcal $mole^{-1}$.[2] A previous value, $-550·7$ kcal $mole^{-1}$, was calculated[292] from heat of solution determinations in nitric acid.[750] Heat-content measurements have been made for the crystals up to the melting point and for the glass up to 1100°C.[783] Heat capacity, entropy, free-energy function, enthalpy, heat of formation and free energy of formation for the 1:3 crystals have been calculated and tabulated from 298 to 2000 K.[1085] Another tabulation of these quantities, at temperatures from 298 K to the melting point, was based on later experimental determinations of enthalpy and gives somewhat different values.[1016]

The β-form, metastable, melts congruently at 728°C[366] (or 740°C[570]); the γ-form melts at 735°C.[570] The *X*-ray diffraction patterns of these forms have been reported.[570]

DISODIUM OCTABORATE, $Na_2B_8O_{13}$ OR $Na_2O,4B_2O_3$

The 1:4 compound occurs in two forms.[570, 581] The usual form is the stable monoclinic[450] form, *d* 2·32[450], which melts congruently at 816°C.[581] A metastable form (m.p. 797°C[366] or 717°C[570]), crystallizing in thin blades, appears in several days if the temperature of heating is below 600°C.[107] Occasionally it is formed at temperatures up to 700°C.[581] Optical properties[176, 581] and *X*-ray diffraction patterns[107, 135, 176] of both forms have been published. The low-temperature form did not change in 2 h at 630°C, but at 685°C the crystals were about half changed to the high-temperature form. After 30 min at 770°C the low-temperature form had disappeared.[581] The 1:4 compound has crystallized from Na_2O–B_2O_3 glasses containing as much as 99% of boric oxide. The eutectic between disodium octaborate and crystalline boric oxide has not been determined, as boric oxide does not crystallize in the system Na_2O–B_2O_3.[581]

The structure of the high-temperature form of the 1:4 compound[349, 450], consists of two independent networks made of 6-membered rings of alternate boron and oxygen. Some of these rings share a tetrahedral boron atom to form a double-ring group. Single rings are linked only to double-ring groups and double-ring groups are linked only to single rings. Non-ring oxygen atoms form bridges between rings to produce a three-dimensional network. One-fourth of the boron atoms are tetrahedrally coordinated with oxygen, the rest being in triangular coordination.[349] The structure has been discussed in terms of the 'structon' theory.[1247] Arguments have been given for a cage structure.[220]

From the heat of solution of the 1:4 compound in hydrochloric acid, its heat of formation has been calculated[2] to be $-1412{\cdot}5$ kcal mole^{-1}. From experimental determinations of enthalpy and other information from the literature, the heat capacity, entropy, free-energy function, enthalpy, heat of formation and free energy of formation have been tabulated for the 1:4 crystals from 298 K to the melting point.[1016] Previous values of the enthalpy and entropy were tabulated for the crystals from 100°C to the melting point and for the glass and liquid from 100° to 1100°C.[780, 783] The 1:4 compound can apparently exist in equilibrium with its saturated aqueous solution between 374° and 600°C. The vapour pressures of the saturated solutions are 47, 85, 136 and 150 bars at 374°, 400°, 500° and 600°C respectively.[580] The crystalline 1:4 compound takes up water from the atmosphere more slowly than the 1:2 or 1:3 compounds or the glassy 1:4 compound.[976, 1060]

SODIUM PENTABORATE, NaB_5O_8 OR $Na_2O,5B_2O_3$

Two kinds of heating curves were observed with a material of composition $Na_2O,5B_2O_5$ prepared by the dehydration of sodium pentaborate pentahydrate, $NaB_5O_8,5H_2O$.[108] Usually a heat effect attributed to the stable form of the 1:4 compound was observed at 810°C, but in certain cases, after reheating for several days, a plateau at 720°C was observed in the heating curve. This was attributed to the possibly incongruent melting of $Na_2O,5B_2O_3$ to give $Na_2O,4B_2O_3$ plus a liquid containing 89% of boric oxide.[108] Heating curves of samples of the 1:5 composition which had been heated for long periods at different temperatures were interpreted as indicating the existence of three allotropic forms, the γ-form changing to the β-form at 720°, the β-form changing to the α-form at 770°, and the α-form melting incongruently at 785°C. The *X*-ray diffraction patterns of these three supposed varieties of the 1:5 compound could not be obtained; at room temperature all the samples studied gave only the pattern of the stable α-1:4 compound.[570]

SODIUM ENNEABORATE, NaB_9O_{14} OR $Na_2O,9B_2O_3$

Three forms of the 1:9 compound have been reported.[570] According to heating-curve studies, the γ-form changes at 325°C to the β-form, which changes at 643°C to the α-form. The α-form melts incongruently at 682°C to form the γ-1:5 compound and a liquid containing 87% of boric oxide.[570] *X*-Ray diffraction patterns of the three forms have been published.[570] Crystallization of the 1:9 compound is slow; after rapid cooling to avoid formation of the 1:4 compound, almost a month of heating at about 550°C was necessary for crystallization.[570]

HYDRATED POTASSIUM BORATES

Phase Equilibria in the System K_2O–B_2O_3–H_2O

Studies of phase equilibrium in the K_2O–B_2O_3–H_2O system have been reported in Mellor, V, 77 and several further studies have been undertaken since.[69A, 143, 147, 217, 705, 711, 840, 841–3, 843A, 1082] Solubility isotherms have been determined at −40° to −5°C[69A, 842]; 0°[842]; 25°[863A]; 35°, 47°, 56°, 80°, 100°, 131°, and 143°C[69A, 840, 843A]; and at 5°; 25°; 45°; 85°; and 95°C.[143, 146–7] A polythermic

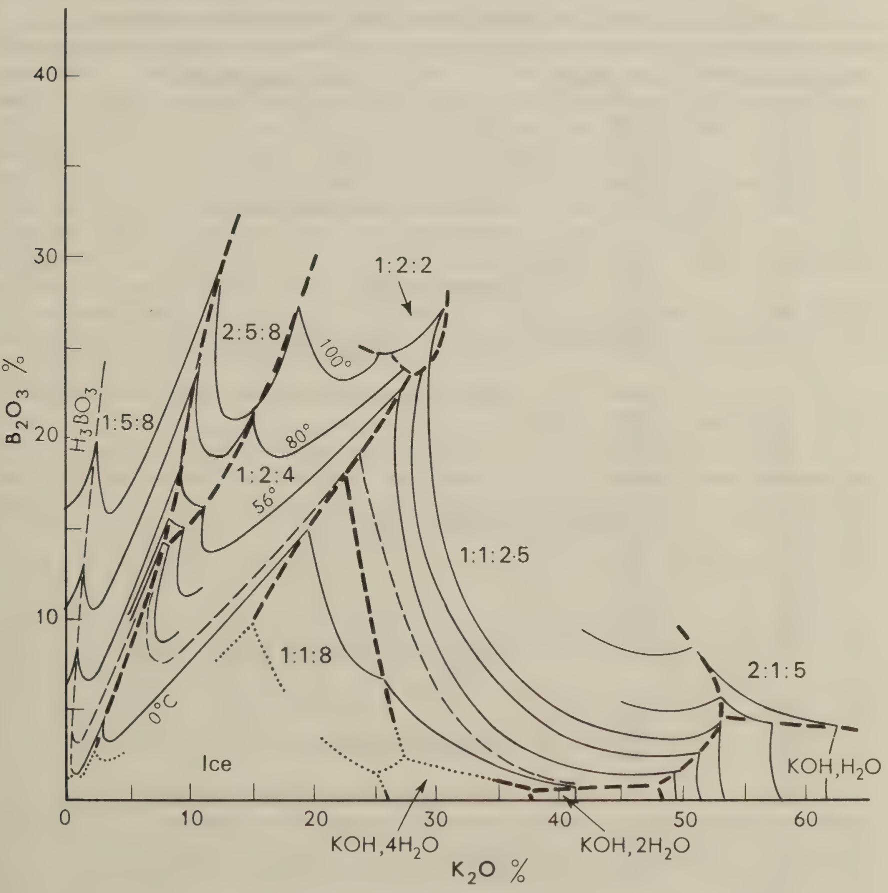

FIG. 11.—Phase diagram for the system K_2O–B_2O_3–H_2O at 0–100°C

diagram showing the fields of the common potassium borates is given in Fig. 11. Diagrams showing the isotherms and stability regions of the known compounds between −40° and 0°C have been published, listing low-temperature eutectics and peritectics.[69A, 841, 843] A ternary eutectic, m.p. −66·5°C, exists at 25·75 wt-% K_2O and 0·80 wt-% B_2O_3.[69A, 842] The temperature at which a solution can be saturated with the three compounds with the $K_2O:B_2O_3:H_2O$ molar proportions 1:2:4, 2:5:5, and 1:5:8 has been reported to be 52·5 ± 2·5°C.[146] More recent studies have been made in which new phases have been crystallized from aqueous solutions by using seed crystals made by dehydration of hydrated borates or by the reaction of potassium hydroxide and boric acid in alcohol.[843A] The 56°, 80° and 100°C isotherms and the polythermal phase diagrams for the K_2O–B_2O_3–H_2O system have been revised to show the fields of the 2:9:11, 1:5:4, 1:2:2, 1:2:3 and 1:5:4 compounds[843A], which did not appear in earlier work.

Tetrapotassium Diborate Hydrate

TETRAPOTASSIUM DIBORATE PENTAHYDRATE, $K_4B_2O_5,5H_2O$ OR $2K_2O,B_2O_3,5H_2O$

The 2:1:5 compound has been crystallized from very concentrated alkaline liquors at 131° and 143°C, but not at 100°C. Its solubility is incongruent.[705, 840] It contains much more water of crystallization than the corresponding sodium salt and is in equilibrium with solutions in a higher temperature range.[840]

Table XII.—Solubilities in the System Potassium Metaborate–Water

Temperature, °C	wt-% KBO_2	Solid-phase details
−5	12·8	Ice
−8	17·6	
−10	20·0	
−13	22·9	
−20	27·1	Eutectic, α-$KBO_2,4H_2O$ and ice
−18	26·6	α-$KBO_2,4H_2O$
−11	30·2	
0	34·2	
10	38·2	
11	39·0	
24	43·8	Transition, α-$KBO_2,4H_2O$ to $KBO_2,1\frac{1}{4}$ or $1\frac{1}{3}H_2O$
0	35·5	$KBO_2,1\frac{1}{4}$ or $1\frac{1}{3}H_2O$ (metastable)
30	44·4	$KBO_2,1\frac{1}{4}$ or $1\frac{1}{3}H_2O$
50	46·4	
56	47·0	
80	49·6	
100	51·6	
120·4	55·8 (b.p.)	
130	56·8	
145	59·4	
150	60·6	
165	65·8	
180	68·8	
195	73·0	Transition, $KBO_2,1\frac{1}{4}$ or $1\frac{1}{3}H_2O$ to $KBO_2,\frac{1}{4}$ or $\frac{1}{3}H_2O$
200	73·1	$KBO_2,\frac{1}{4}$ or $\frac{1}{3}H_2O$
223	74·2	
236	74·0	
237	73·4	
250	74·0	Transition, $KBO_2,\frac{1}{4}$ or $\frac{1}{3}H_2O$ to anhyd. KBO_2
256	73·8	KBO_2
277	73·2	
300	73·0	

Potassium Metaborate Hydrates

SOLUBILITY

Solubilities in the KBO_2–H_2O system have been reported[840–1, 1082] and are presented in Table XII. From solubility determinations and heating curves determined under pressure, a phase diagram has been constructed for the KBO_2–H_2O system from −20° to 300°C.[840] Other investigators have reported a different solubility curve with an ice–KBO_2,H_2O eutectic at 37·5 wt-% KBO_2, m.p. −13·5°C, and a KBO_2,H_2O–KBO_2 transition point at 30°C, 41·55 wt-% KBO_2.[217] Comparison of this curve with previous work[840] suggests that the eutectic reported at −13·5°C may be metastable with respect to the 1:1:8 compound. The reported[217] transition to anhydrous KBO_2 at 30°C appears to be incorrect.

POTASSIUM METABORATE 4½-HYDRATE, $KBO_2,4\frac{1}{2}H_2O$ OR $K_2O,B_2O_3,9H_2O$

The 1:1:9 compound did not appear in the solubility studies reported above, but was found later to be the stable metaborate phase at 0°C in the system K_2O–B_2O_3–H_2O. Its isotherm at this temperature is between those of the 1:2:4 and the 1:1:2·5 compounds[842]; it is nearly parallel to the isotherms of the α-1:1:8 and β-1:1:8 compounds and somewhat below them.[842]

POTASSIUM METABORATE TETRAHYDRATE, $KBO_2,4H_2O$ OR $K_2O,B_2O_3,8H_2O$

As shown in the above solubility data, the α-1:1:8 compound has been reported to be in equilibrium with its solution from the cryohydric point to 24°C.[840–1] Later, the β-form was discovered, having an isotherm at 0°C nearly parallel to that of the α-form and slightly below it.[842] The α-form is therefore metastable with respect to the β-form at this temperature. Both α- and β-forms are metastable with respect to the 1:1:9 compound at 0°C. The β-form crystallizes after about 48 h agitation from a K_2O–B_2O_3–H_2O solution slightly more alkaline than metaborate, and slightly unsaturated with $K_2O,B_2O_3,2{\cdot}5H_2O$, at temperatures between 0° and −10°C.[842] The fields of the α- and β-forms have been determined at temperatures below 0°C.[842] DTA studies (cooling) have indicated that the transition point is close to −30°C along the whole length of the −30° metaborate isotherm.[842] The β-form has an incongruent solubility below 0°C.[69A] To obtain seeds of the α-form, prolonged agitation for several hours near −60°C was necessary.[841]

Thermogravimetric analysis of the β-form of the 1:1:9 compound did not show any definite intermediate stages during the loss of the eight molecules of water.[69A]

POTASSIUM METABORATE 1¼ OR 1⅓ HYDRATE, $KBO_2,1\frac{1}{4}$ OR $1\frac{1}{3}H_2O$

The 1:1:2·5 (or 1:1:2⅔) compound, orthorhombic[634, 946], crystallizes in the K_2O–B_2O_3–H_2O system at temperatures as low as −20°C and as high as 143°C.[840, 843] The crystal structure of a hydrated potassium monoborate has recently been reported.[947A] In contact with its own solution, it has been reported stable from 24° to 195°C.[841] Its *X*-ray diffraction pattern has been published[844], and its unit-cell dimensions have been measured.[634, 946] Infra-red studies, using compounds containing boron and hydrogen isotopes, show that the 1¼-hydrate and the ¼-hydrate (regarded as the 1⅓- and ⅓-hydrates by the authors) contain both three- and four-coordinated boron.[393] The 1¼-hydrate is quite hygroscopic[559, 634]; its water of hydration has been reported as 1¼ molecules[840, 1082] (Mellor, V, 77), 1⅓ molecules[479, 634, 946] and 1½ molecules.[249] The formula $K_3B_3O_3(OH)_6,H_2O$ has been proposed, based on the 1⅓-hydrate composition.[478] N.m.r. studies do not disagree with this formula but suggest that a greater water content and a smaller OH content are more probable.[362]

In one investigation, the salt, regarded as the 1⅓ hydrate, lost one molecule of water at 100°C (which it quickly regained in moist air) and was said to be dehydrated to the anhydrous salt above 160°C.[479] These changes were studied by *X*-ray and infra-red methods.[478] In another study, a thermogravimetric curve of the 1¼-hydrate[840] indicated that this compound lost no water, under the conditions used, at temperatures up to 164°C. It then lost one molecule rapidly, and the composition remained constant at $\frac{1}{4}$ molecule of water between 195° and 224°C. Between 224° and 230°C about 0·15 molecule more was lost; and the last 0·1 molecule was lost gradually between 230° and 450°C.[840]

When adhering moisture was present (1·5 molecules total water content) potassium metaborate attacked glass.[559]

POTASSIUM METABORATE $\frac{1}{4}$- OR $\frac{1}{3}$-HYDRATE, $KBO_2,\frac{1}{4}$ OR $\frac{1}{3}H_2O$

The $\frac{1}{4}$-hydrate crystallizes from solution at temperatures between 195° and 250°C, according to solubility and heating-curve measurements under pressure.[840–1] It has also been regarded as a $\frac{1}{3}$-hydrate[478], and the structural formula $\{K_3[B_3O_5(OH)_2]\}_n$ has been proposed.[478] N.m.r. studies[362] agree with this formula. Its *X*-ray diffraction pattern has been published.[844] Solubility data for this hydrate appear in Table XII.

Dipotassium Tetraborate Hydrates

SOLUBILITY

Although the 1:2:4 compound becomes metastable with respect to the 2:5:5 compound in contact with its solution above 56°C[844] the 2:5:5 compound is very slow to crystallize in the absence of seed, and the solubility of the 1:2:4 compound may be determined at temperatures up to above 100°C. Solubility determinations are reported, from four sources[510, 727, 840, 1082], in Table XIII. Figures from two of these sources[727, 1082] have been recalculated to give the solubilities in wt-% $K_2B_4O_7$ throughout. Other studies of the solubility have been made.[1134A]

Table XIII.—Solubility of Dipotassium Tetraborate, $K_2B_4O_7$, *in Water*

(Solubilities stated in wt-% $K_2B_4O_7$; solid phase throughout is $K_2B_4O_7,4H_2O$)

Temperature, °C	Solubility	Temperature, °C	Solubility
−3	5·8[840] (cryohydric point)	47	22·7[840]
0	7·0[840], 6·2[727], 6·41[1082]	50	24·3[727], 23·54[1082], 23·4[510]
9·3	8·54[1082]	56	27·6[840]
15	10·1[727]	60	28·2[727], 28·12[1082], 28·2[510]
16	10·51[1082]	70·8	33·59[1082]
20	12·3[840], 11·9[727], 12·13[1082], 11·5[510]	80	37·7[840]
25	13·7[727]	81	38·44[1082]
30	15·5[840], 15·25[1082], 15·2[510]	100	46·4[840]
35	17·1[840], 17·7[727], 17·20[1082]	105·4	50·91[1082] (b.p.)
40	19·3[840], 19·44[1082], 19·2[510]		

DIPOTASSIUM TETRABORATE OCTAHYDRATE, $K_2B_4O_7,8H_2O$ OR $K_2O,2B_2O_3,8H_2O$

The 1:2:8 compound was prepared by early investigators[559], but it did not appear in later studies.[840, 842, 843A] Over sulphuric acid 7·39 molecules of water were lost gradually, during 226 days.[559]

DIPOTASSIUM TETRABORATE PENTAHYDRATE, $K_2B_4O_7,5H_2O$ OR $K_2O,2B_2O_3,5H_2O$

The existence of the 1:2:5 compound mentioned in early investigations (Mellor, V, 77) is doubtful. A new 1:2:5 compound has, however, been reported recently.[842–3] Seed crystals for crystallization of the new 1:2:5 compound were made by prolonged agitation or by the addition of alcohol. The 0°C [842] and 100°C [843] isotherms of the new 1:2:5 compound in the K_2O–B_2O_3–H_2O system have been determined, and its *X*-ray diffraction pattern has been published.[843] This pattern is different from that given for the pentahydrate on card 1-195 of the Powder Diffraction File[1114A], which appears to be the pattern of the 1:5:8 compound instead. This suggests that the infra-red spectrum[568] said to be that of the 1:2:5 compound may also have been incorrectly identified.

A thermogravimetric study of the new 1:2:5 compound showed two plateaux, corresponding to the trihydrate at 150°C and to the monohydrate at 300°C.[843]

DIPOTASSIUM TETRABORATE TETRAHYDRATE, $K_2B_4O_7,4H_2O$ OR $K_2O,2B_2O_3,4H_2O$

The 1:2:4 compound is the most common hydrate of dipotassium tetraborate. It is orthorhombic, *d* 1·945[309] or 1·919.[531] The structure[531,728] has a unit cell containing four $K_2[B_4O_5(OH)_4],2H_2O$ units. The polyborate ion, $[B_4O_5(OH)_4]^{2-}$, is like that found[584] in borax, consisting of two BO_3OH and two BO_2OH groups sharing oxygen atoms to form a two-ring structure (Fig. 5), with which n.m.r. studies agree.[362] The *X*-ray diffraction pattern has been published.[844] The electrical conductivity, measured during heating of the sample, showed a small peak at 450°C and a large increase from 500°C to 745°C.[811]

A study of solution rates as a function of temperature and concentration indicated that dissolution of the 1:2:4 compound is rapid. In 100 s at 49°C with mild agitation, 90% of saturation was reached.[1134A]

Thermal analysis under pressure indicates that the tetrahydrate in contact with its saturated solution decomposes at 145°C to give a dihydrate and a liquid containing about 63 wt-% of $K_2B_4O_7$.[840] The heating curves under pressure also indicate a change from $K_2O,2B_2O_3,2H_2O$ to $K_2O,2B_2O_3,H_2O$ at 240°C in contact with a liquid containing about 72 wt-% of $K_2B_4O_7$, and a change from the monohydrate to the anhydrous salt at 300°C in contact with a liquid containing about 75 wt-% of $K_2B_4O_7$.[840]

Dehydration

Heating a 5-g sample of the 1:2:4 compound in an oven for 5-h periods at the successive temperatures given resulted in the following percentage losses in weight: 75° 0·07; 85° 0·13; 95° 1·13; 105° 1·44; 115° 2·14; 145° 13·72; 165° 15·82; 205° 18·39; 250° 21·07; 300° 22·9.[727] This compound has been recommended as a primary standard for standardizing of acids.[727]

The differential thermal curve[493,811] showed endothermic effects at 180° and 800°C and an exothermic effect at 450°C. The thermogravimetric curve showed a loss of two molecules of water between 112° and 180°C and loss of the last two molecules gradually between 180° and 420°C.[811] Heated *in vacuo*, $K_2O,2B_2O_3,4H_2O$ was stable up to 100°C, where half its water was rapidly lost. The last two molecules were lost gradually at temperatures up to 400°C.[307] In atmospheres saturated with water vapour at 90°[840] and 95°C[309], thermogravimetric curves for $K_2O,2B_2O_3,4H_2O$ indicated that two molecules of water were lost between 112° and 140°C, one more between 200° and 230°C, and the last between 250° and 290°.[309] Thus there were plateaux at 140°–200°C and 230°–250°C, corresponding to the 1:1:2 and 1:2:1 compounds. The plateaux did not appear at low humidities. The change from $K_2B_4O_7,4H_2O$ to $K_2B_4O_7,2H_2O$ was reversible.[309] In air saturated with water vapour at 20°C, two molecules of water were lost on heating from 112–130°C and the last two were lost between 130° and 400°C.[309] The anhydrous state was thus reached more quickly and at a lower temperature if the humidity of the atmosphere was high.[309] The temperature of the beginning of water loss from $K_2B_4O_7,4H_2O$ increases rapidly with the partial pressure of water vapour in the atmosphere, from 85°C at about 2 mm to a maximum of 111 ± 1°C at about 16 mm. From the slope of this curve, the heat of dehydration to give the dihydrate and water vapour was calculated to be 20·7 kcal mole^{-1} of water.[309]

DIPOTASSIUM TETRABORATE TRIHYDRATE, $K_2B_4O_7,3H_2O$ OR $K_2O,2B_2O_3,3H_2O$

The 1:2:3 compound is a stable phase in the ternary system at temperatures from about 52° to above 100°C.[843] Its powder diffraction pattern, solubility isotherms at 56°, 80° and 100°C and its region of stability have been reported.[843,843A] Its solubility is incongruent.[843]

DIPOTASSIUM TETRABORATE DIHYDRATE, $K_2B_4O_7,2H_2O$ OR $K_2O,2B_2O_3,2H_2O$

The 1:2:2 compound, *d* 2·14[309], is formed by heating the 1:2:4 compound in air saturated at 90°C[840] or at 95°C[309] with water vapour, as mentioned above, or by crystallization from more alkaline solutions. Heating-curve studies under pressure suggest that the 1:2:2 compound, formed from the 1:2:4 compound at 145°C, decomposes at 240°C to give the 1:2:1 compound and a solution containing about 72 wt-% of $K_2B_4O_7$.[840] The powder diffraction pattern of the 1:2:2 compound has been published.[844] A photograph of the crystals suggests that they may be orthorhombic.[309] Its solubility is incongruent.[844] Its 80° and 100°C isotherms have been determined[840, 843]; the 100°C isotherm is metastable with respect to the 1:2:3 compound.[843] Crystals having the 1:2:2 composition made from trimethylborate and potassium ethoxide are very hygroscopic.[321]

DIPOTASSIUM TETRABORATE MONOHYDRATE, $K_2B_4O_7,H_2O$ OR $K_2O,2B_2O_3,H_2O$

The 1:2:1 compound, *d* 2·10[309], was formed between 140° and 200°C in a thermogravimetric study of the tetrahydrate in air of high humidity.[309] Heating curves and solubility studies under pressure have indicated that it is in equilibrium with its solution between 240° and 300°C[840] and that at 300°C, under pressure, it decomposes to form the anhydrous salt and a solution containing approximately 75 wt-% of $K_2B_4O_7$.[840]

Potassium Triborate Hydrates, $KB_3O_5,1\frac{1}{2}H_2O$ and $KB_3O_5,2H_2O$, or $K_2O,3B_2O_3,3H_2O$ and $K_2O,3B_2O_3,4H_2O$

The 1:3:3 compound has been crystallized in the K_2O–B_2O_3–H_2O system at 100°C, and its 100° isotherm (metastable) has been determined.[843A]

The 1:3:4 compound, made from trimethylborate and potassium alkoxide, is very hygroscopic.[321] Its *X*-ray diffraction pattern has been published, and n.m.r. measurements have indicated that its water content is in the form of OH groups.[321]

Tetrapotassium Decaborate Hydrates

TETRAPOTASSIUM DECABORATE HEXAHYDRATE, $K_4B_{10}O_{17},6H_2O$ OR $2K_2O,5B_2O_3,6H_2O$

The 2:5:6 compound, first reported in 1970, does not crystallize spontaneously from solutions in the K_2O–B_2O_3–H_2O system, but was crystallized by using seed prepared separately in various ways. Its 100°C isotherm, which is partly metastable, was determined.[843A]

TETRAPOTASSIUM DECABORATE PENTAHYDRATE, AUGER'S POTASSIUM BORATE, $K_4B_{10}O_{17},5H_2O$ OR $2K_2O,5B_2O_3,5H_2O$

The 2:5:5 compound, orthorhombic, *d* 2·15[146], was first prepared by Auger, in 1925.[36] Its *X*-ray diffraction photographs have been published.[146, 844] The crystal structure[526] contains $[B_5O_8(OH)]^{2-}$ units composed of a central tetrahedral boron atom with two opposite edges shared with a B_2O_5 group on one side and a $B_2O_5(OH)$ group on the other. The B_2O_5 group consists of two BO_3 triangles, and the $B_2O_5(OH)$ group consists of one BO_4 tetrahedron and one BO_2OH triangle. The unit is thus similar to the two-ring pentaborate ions found in potassium pentaborate[933], which are bonded to other ions by hydrogen bonds. The $[B_5O_8(OH)]^{2-}$ units in Auger's potassium borate, however, are bonded to four other similar groups by sharing four oxygen atoms, and are also held together by K–O bonds and hydrogen bonds.[526] The position and bonding of the two water molecules of the $K_2[B_5O_8(OH)],2H_2O$ compound are such that they can be lost without any major change in the structure, thus explaining the reversible loss and regain of four-fifths of its water content.[146, 526]

The solubility of the 2:5:5 compound, congruent above 40°C, has been determined[840]; values are given in Table XIV.

Table XIV.—Solubility in Water of $K_4B_{10}O_{17},5H_2O$ (*Auger's Potassium Borate*)[840]

(Solubilities in wt-% of $K_4B_{10}O_{17}$)

Temperature, °C	Solubility	Temperature, °C	Solubility
40	23·2	180	48·4
47	24·2	190	50·0
56	26·2	200	51·6
70	28·6	220	56·0
80	31·0	240	58·4
100	33·8	260	62·7
120	37·2	272	65·0
135	40·0	280	66·8
152	43·0	300	71·4
173	46·8	330	80·0

The 2:5:5 compound is a stable phase in the K_2O–B_2O_3–H_2O system at temperatures as low as 28 ± 3°C.[840] At 100°C, in contact with solutions having $K_2O:B_2O_3$ molar ratios between 0·35 and 0·5, it is metastable with respect to the 2:5:6 compound.[843A]

Photomicrographs of the 2:5:5 crystals have been published.[146] The crystals are usually very small, but have been obtained about 1 mm long.[146] Although they are metastable at room temperature, they can be kept in contact with their mother liquor at room temperature for a month or more[147], in the absence of other crystals. A reported '7-hydrate'[144] was later found to be the 5-hydrate.[146–7]

Dehydration

Auger reported a loss of four molecules of water between 40° and 100°C.[36] Thermogravimetric curves have been studied[146–7, 840] by using crystals having mean lengths of 0·02 and 0·5 mm and several successive cycles of dehydration-rehydration in air saturated with water at 25°C. The 0·5-mm crystals gave more satisfactory curves, with inflections indicating the formation of the 2:5:3 compound at 140°C and the 2:5:1 compound at 360°C[146] or 256–400°C.[840] The first four molecules of water are therefore lost much more easily than the last molecule. If the dehydration was stopped at this point, rehydration on cooling gave an inflection at the 2:5:3 composition at 100–120°C.[146] The salt was completely dehydrated to form a product with a higher density, 2·23, by heating to about 450°C[146] or 480–500°C.[840] When so treated, it did not begin to rehydrate until cooled to 35°C, and the rehydration curve did not show an inflection.[146] The dehydration and rehydration behaviour agrees with the presence of the $[B_5O_8OH]_n^{2n-}$ polyion in the 2:5:5, 2:5:3 and 2:5:1 compounds.[840] Crystals of the 2:5:5 compound, when made from trimethyl borate and potassium ethoxide, are very hygroscopic.[321]

TETRAPOTASSIUM DECABORATE TRIHYDRATE, $K_4B_{10}O_{17},3H_2O$ OR $2K_2O,5B_2O_3,3H_2O$

The 2:5:3 compound, *d* 2·09 ± 0·01[146] was formed at 140°C in the thermogravimetric studies of the 5-hydrate[146–7, 840] referred to above; it did not crystallize from solution, however, in a heating-curve and solubility study under pressure.[840] It is readily hydrated back to the 5-hydrate in humid air, and can be dehydrated to the 1-hydrate by heating to a temperature between 256° and 400°C.[840]

TETRAPOTASSIUM DECABORATE MONOHYDRATE, $K_4B_{10}O_{17},H_2O$ OR $2K_2O,5B_2O_3,H_2O$

The 2:5:1 compound, *d* 1·97, formed by heating the 5-hydrate to about 300–400°C[146] (or 260–390°C)[840], takes up water vapour from the atmosphere to form the 2:5:3 and 2:5:5 compounds.[146] The rehydration curve in air saturated with water vapour at 25°C shows an inflection corresponding to the 2:5:3 compound, at 120°C.[146] Heating curves and solubility studies under pressure have been interpreted to indicate that the 2:5:5 compound decomposes at 330°C to form the 2:5:1 compound and a saturated solution containing 80·0 wt-% of $K_4B_{10}O_{17}$.[840]

DIPOTASSIUM OCTABORATE HEXAHYDRATE, $K_2B_8O_{13},6H_2O$ OR $K_2O,4B_2O_3,6H_2O$

The 1:4:6 compound has been crystallized in the K_2O–B_2O_3–H_2O system and its 100°C isotherm, which is metastable, was determined.[843A]

DIPOTASSIUM ENNEABORATE UNDECAHYDRATE, $K_4B_{18}O_{29},11H_2O$ OR $2K_2O,9B_2O_3,11H_2O$

The 2:9:11 compound is in equilibrium with solutions at temperatures from about 56° to 100°C in the K_2O–B_2O_3–H_2O system, and its isotherms and crystallization regions have been determined.[843A] A large part of its region of crystallization is metastable.[843A]

Potassium Pentaborate Hydrates

SOLUBILITY

Solubilities in the system KB_5O_8–H_2O summarized from several sources[306, 559, 562, 700, 843A, 1082] are presented in Table XV; where necessary, values have been recalculated to express all solubilities uniformly in wt-% of KB_5O_8. Solubility values for the recently discovered tetrahydrate, $K_2O,5B_2O_3,4H_2O$ are included at the end of Table XV. Below 46°C, the solubility of the 1:5:8 compound is less than that of the 1:5:4 compound, indicating that the 1:5:8 compound is more stable than 1:5:4 below that temperature, whereas the 1:5:4 compound is the more stable above it.[843A] In a study of the metastable solubility of the α-1:5:8 compound above 100°C, another form (β) of the 1:5:8 compound was found to be more stable than the α-form between 149° and 168°C.[1200A] Both α- and β-forms are metastable with respect to the 1:5:4 compound in this region. A phase diagram of the KB_5O_8–H_2O system from 100° to 368°C has been published.[1200A] The presence of sufficient ammonium chloride decreases the solubility of the 1:5:8 compound by 20–30%.[306]

Table XV.—Solubility of KB_5O_8 *in Water*

(Solubilities expressed as wt-% of KB_5O_8)

Temperature, °C	Solubility	Solid phase	Temperature, °C	Solubility	Solid phase
−0·52	1·53[562]	α-$KB_5O_8,4H_2O$ and ice	150	43·4[840]	α-$KB_5O_8,4H_2O$
0	1·75[1082] 1·55[843A]	α-$KB_5O_8,4H_2O$	160	47·6[840]	,,
5	1·77[700]	,,	165	51·0[840]	(Transition)
5·5	2·00[1082]	,,	190	53·0[840]	KB_5O_8,H_2O
9·3	2·30[1082]	,,	212	55·6[840]	,,
16·0	2·57[1082]	,,	230	59·6[840]	,,
18	2·754[559] 2·7[306]	,,	247	61·8[840]	,,
20	2·7[700]	,,	252	63·1[840]	,,
25	3·412[559]	,,	265	66·0[840]	(Transition)
30	3·80[700] 4·40[843A]	,,	265	62·8[840]	$KB_5O_8,0·5H_2O$
35	4·75[1082]	,,	268	59·6[840]	,,
40	5·22[1082]	,,	279	51·4[840]	,,
45	5·71[700]	,,	285	46·2[840]	,,
50	6·75[1082]	,,	300	40·0[840]	,,
56	8·30[843A]	,,			
65	9·75[1082]	,,	0	2·00[843A]	$KB_5O_8,2H_2O$
70·8	11·36[1082]	,,	30	3·85[843A]	,,
80	14·56[1082] 15·1[840]	,,	46	5·70[843A]	,,
100	21·2[843A]	,,	56	7·25[843A]	,,
101	25·22[1082] (b.p.)	,,	80	10·65[843A]	,,
130	35·6[840]	,,	100	15·25[843A]	,,

POTASSIUM PENTABORATE TETRAHYDRATE, $KB_5O_8,4H_2O$ OR $K_2O,5B_2O_3,8H_2O$

The α-1:5:8 compound is the best known hydrate of potassium pentaborate. It crystallizes in orthorhombic prisms[693], with *d* 1·74[172, 182, 309], and Mohs hardness 2½. *X*-Ray powder diffraction patterns have been published.[172, 844] Crystal structure studies[182, 782, 930, 933] have shown that the borate ion structural unit consists of two perpendicular trimeric boron–oxygen rings sharing a common tetrahedral boron atom. The other boron atoms are in trigonal coordination. The hydrogen atoms have been located by neutron diffraction.[34A] The proton–proton distances and the orientation of the water molecules in the crystal have been determined.[545] N.m.r. studies have shown resonance from both trigonal and tetrahedral boron atoms.[119] N.m.r. data[362, 472, 782] and a proton magnetic resonance study[774] agreed with the crystal structure. The infra-red absorption spectrum has been studied.[1239, 315] Elastic, piezoelectric, and dielectric coefficients have been published.[182] The specific magnetic susceptibilities of the 1:5:8 compound, and products made by dehydration to two, one and zero molecules water content, have been found to be $-0{\cdot}500$, $-0{\cdot}455$, $-0{\cdot}423$, and $-0{\cdot}394 \times 10^{-6}$ c.g.s. units, respectively.[663] The heat capacity has been determined from 17·6 to 368°K and the entropy and other thermal functions tabulated from 0 to 373°K.[266] At 298·15°K the heat capacity is 330·48 J deg^{-1} $mole^{-1}$ ($KB_5O_8,4H_2O$).[266] At about 5 kilobars there is a transition to a high-pressure form which has been characterized by powder *X*-ray diffraction.[4] Compressibility data have been reported for pressures up to 40,000 kg cm^{-2}.[120A]

Dehydration

Over sulphuric acid at room temperature, the 1:5:8 compound loses practically no water in 276 days.[559] At 210°C in an oven it loses 20·79% in weight, and at 400°C it loses 25·73%, but some of this consists of volatilized boric acid.[249] If the 1:5:8 compound is heated at 20°C per h in contact with air which has been saturated with water at 20°C, dehydration begins at 120°C and six molecules of water are lost between 120° and 170°C; the last two molecules are gradually lost as the temperature is increased to 450°C. If the atmosphere has been saturated with water at 90°C, however, dehydration does not begin until the temperature reaches 170°C, and the first six molecules of water are lost by about 200°C. The weight loss then remains almost constant until further loss of weight begins at 260°C.[309] This plateau is displaced because of loss of some boric oxide volatilization. The anhydrous salt (*d* 1·92) takes up moisture readily from air saturated at 22°C to form the original 8-hydrate.[309]

In a current of nitrogen having a partial pressure of water vapour of 14 mm of mercury, slow dehydration began at 107°C. At 150°C, in several hours, 70 to 73% of the water content was lost. At 170°, 75% was lost, and at 190°C, 87%; complete dehydration was reached at 250°C.[693] By plotting the temperature of the beginning of dehydration against the partial pressure of water vapour, the heat of dehydration was calculated to be 26·5 kcal $mole^{-1}$ between 106·5° and 134°C.[309]

A thermogravimetric curve showed a rapid loss of about seven molecules of water between 130° and 260°C and loss of the last molecule at temperatures up to 400°C.[811] Thermogravimetric curves have been determined for samples of the 1:5:8 compound crystallized at different temperatures. After crystallization at a low temperature, the dehydration curve is smooth, but after the sample has been crystallized at 100°C, the α–β transformation takes place, and there are irregularities in the curve.[1200A] When heated *in vacuo*, the 1:5:8 compound is stable up to 105°C, where six molecules of water are lost. The last two molecules are lost gradually at higher temperatures.[307]

POTASSIUM PENTABORATE DIHYDRATE, $KB_5O_8,2H_2O$ OR $K_2O,5B_2O_3,4H_2O$

The 1:5:4 compound was first crystallized from aqueous solution in 1969. Its *X*-ray diffraction pattern has been published.[1200A] The 80°, 56°, 30° and 0°C isotherms and the large stability region of this compound have been determined in the K_2O–B_2O_3–H_2O system. The 0° and 30°C isotherms and part of the 56°C isotherm are metastable.[843A] The solubility–temperature curve (values given in Table XV), indicates that the 1:5:4 compound is stable in contact with its own solution above 46°C.[843A] Crystals having the 1:5:4 composition, prepared from trimethylborate and potassium alkoxide in an organic solvent, are very hygroscopic and are shown by n.m.r. to contain water only in the form of OH groups.[321]

A thermogravimetric curve has plateaux at water contents of two and one molecule.[1200A]

POTASSIUM PENTABORATE MONOHYDRATE, KB_5O_8,H_2O OR $K_2O,5B_2O_3,2H_2O$

The *X*-ray diffraction pattern of the 1:5:2 compound has been published.[1200A] Heating curves and solubility studies under pressure indicate that the 1:5:2 compound is in equilibrium with its solution between 165° and 265°C.[840] Its solubility is recorded in Table XV. In an atmosphere saturated with water vapour at 90°C, a plateau appeared in the heating curve at the 1:5:2 composition.[309, 840]

POTASSIUM PENTABORATE HEMIHYDRATE, $KB_5O_8,\frac{1}{2}H_2O$ OR $K_2O,5B_2O_3,H_2O$

The *X*-ray diffraction pattern of the 1:5:1 compound has been published.[1200A] Heating curves and solubility studies under pressure indicate that the 1:5:1 compound is in equilibrium with its solution between 265° and 310°C[840], decomposing at 310°C to give the anhydrous salt. Solubility values are given in Table XV. This compound did not appear in thermogravimetric studies of the 1:5:8 compound.

POTASSIUM (1:12) BORATE 5- OR 7-HYDRATE, $K_2B_{24}O_{37},5H_2O$ OR $7H_2O$ OR $K_2O,12B_2O_3,5H_2O$ OR $7H_2O$

A crystalline compound having the 1:12:5 or 1:12:7 composition has been made by adding water dropwise to trimethylborate and potassium alkoxide in an organic solvent. It is very hygroscopic. N.m.r. studies have shown that it contains water only in the form of hydroxyl groups.[321]

Hydrated Double Borates of Potassium

Brief reference is made below to double borates containing potassium, with calcium, strontium, barium, magnesium, zinc, cadmium or cobalt.

Dipotassium calcium octaborate dodecahydrate, $K_2O,CaO,4B_2O_3,12H_2O$, crystallized after a few hours in orthorhombic prisms (d_{25} 1·80[1107A] or 1·793[729]) from a solution of excess of potassium diborate and calcium chloride. Its method of preparation and unit-cell data have been reported.[729] In water its solubility is 7·3 g l^{-1} at 20°C.[283] Its indices of refraction have been determined.[283] When it is heated, exothermic effects occur, which are accompanied by an increase in electrical conductivity. Two molecules of water are lost at 100–110°C, eight more at temperatures up to 200°C, and the remaining two at temperatures up to 620°C.[303] When the dodecahydrate is treated with water at 25°C, $2CaO,3B_2O_3,9H_2O$ is formed.[1241] Infra-red spectra suggest the presence of the polyborate anion $[B_4O_5(OH)_4]^{2-}$, also found in borax.[284A]

Dipotassium strontium octaborate 14-hydrate, $K_2O,SrO,4B_2O_3,14H_2O$, *d* 1·936[729] has properties similar to those of the dipotassium calcium octaborate.[1107A] Its unit-cell data have been determined.[729]

Dipotassium barium octaborate 14-hydrate, $K_2O,BaO,4B_2O_3,14H_2O$, orthorhombic, (*d* 2·04[387], or 2·027[729]), is metastable and decomposes slowly in water to give barium tetraborate. It loses ten molecules of water at temperatures below 65°C.[387]

Dipotassium magnesium hexaborate 15-hydrate, $K_2O,MgO,3B_2O_3,15H_2O$ (specific gravity 1·91), loses ten molecules of water at 40–60°C, two molecules more at 60–100°C, and the last three molecules at 100–350°C. Its solubility in water is 10 g l^{-1} at 5–6°C; in 3% boric acid at 10°C it is 40 g l^{-1}.[388]

Kaliborite, $K_2O,4MgO,12B_2O_3,15H_2O$, has a structure containing polyanions of the type $[B_6O_8(OH)_5]^{3-}$ linked along the *b*-axis.[183] *X*-Ray patterns of various specimens have been published.[586] The infra-red absorption spectrum has been determined.[898] This mineral has also been named *paternoite*, but the name *kaliborite* has priority.[586]

Potassium zinc pentaborate pentahydrate, $KZnB_5O_9,5H_2O$ or $K_2O,2ZnO,5B_2O_3,$-$10H_2O$, *d* 2·31, is a white amorphous powder which hydrolyzes slowly[669]; it has been studied by DTA.[669] Between 65° and 75°C 40% of its water is lost; 40% more is lost between 130° and 150°C, and the remainder is lost at temperatures up to 350°C.[1107A]

Dipotassium cadmium dodecaborate decahydrate, $K_2O,CdO,6B_2O_3,10H_2O$, triclinic, *d* 2·13, when heated begins to lose water at about 70°C and is completely dehydrated at 300°C. Its unit-cell dimensions have been determined.[665]

Dipotassium cobalt dodecaborate undecahydrate, $K_2O,CoO,6B_2O_3,11H_2O$, *d* 2·1, forms pink crystals. The structure has been determined.[771A] It is stable in air up to 50°C, and loses nine molecules of water in three steps between 50° and 200°C. The last two molecules are lost at 200°–350°C. The crystals hydrolyze in water. In 3% boric acid solution, the solubility is 7 g l^{-1}.[386]

ANHYDROUS POTASSIUM BORATES

Phase Equilibria in the System K_2O–B_2O_3

Phase equilibrium studies by thermal analysis of compositions between 40 and 90 wt-% B_2O_3[697–8] and between 81 and 96 wt-% B_2O_3[840] have shown the existence of compounds with $K_2O:B_2O_3$ molar ratios of 1:1, 1:2, 1:3, 1:4, 1:5 (three forms) and 1:9. Eutectics have been found at 45·3, 37·5, 33·5 and 21·3 wt-% K_2O, melting at 787°, 770°, 825° and 780°C respectively. If the 1:3 compound does not crystallize, a metastable eutectic at 36·5 wt-% K_2O, m.p. 725°C, is also observed.[698] In a visual-polythermal study, eutectics were observed at 24 and 40 mole-% B_2O_3, with melting points 782° and 780°C.[1212]

Crystalline Anhydrous Potassium Borates

POTASSIUM ORTHOBORATE OR TRIPOTASSIUM BORATE, K_3BO_3 OR $3K_2O,B_2O_3$

Infra-red studies have been made[637A, 744A] on a compound said to be K_3BO_3, but this compound does not appear to have been reported elsewhere.

POTASSIUM METABORATE, KBO_2 OR K_2O,B_2O_3

The 1:1 compound, rhombohedral, *d* 2·32[523A], m.p. 950°[698], 947° (Mellor, V, 77), 968°[177] or 940°C[523A], crystallizes in tables or prisms. Its *X*-ray diffraction pattern has been published.[523A, 844] It is isostructural with sodium metaborate.[736A] The borate ion in potassium metaborate consists of $B_3O_6^{3-}$ rings formed of trigonal BO_3 groups.[736A, 931] A structure refinement indicated that in the potassium and sodium compound the bond strength in this ion does not have a simple relationship to the bond length.[736A] The structure of potassium metaborate has been discussed in terms of the 'structon' theory.[1247] N.m.r. studies have been made[773] and correlated with the coordination state of boron in the structure.[119] The infra-red absorption spectrum[315, 523A, 899] shows some similarity to that of the isostructural sodium compound. The indices of refraction, determined by the immersion method, are N_g 1·531 and N_p 1·486.[523A]

Differential thermal analysis showed four endothermic effects, at 150°, 440°, 780° and 940°C (m.p.).[523A]

The crystals rapidly take up water and carbon dioxide from the air[840]; reaction with moist air gives the composition $K_2O,B_2O_3,2{\cdot}67H_2O$.[478]

TETRAPOTASSIUM HEXABORATE, $K_4B_6O_{11}$ OR $2K_2O,3B_2O_3$

The 2:3 compound (incongruent melting-point 778°C) was reported in a visual-polythermal study of phase equilibria in the $K_2B_4O_7$–KBO_2 system.[875]

DIPOTASSIUM TETRABORATE, $K_2B_4O_7$ OR $K_2O,2B_2O_3$

The 1:2 compound, triclinic, congruent m.p. 815° [698], 780° to 800° [523A], 796°[1212], or 798 ± 5°C[80A], *d* (calc.) 2·53[451], *d* (obs.) 2·17[523A], is a stable phase in the system K_2O–B_2O_3.[698] Its *X*-ray diffraction pattern[80A, 523A, 783, 844] and its infra-red absorption spectrum[523A, 899] have been published. Unit-cell data[451] and the crystal structure[419] have been determined. Indices of refraction have been determined to be N_d 1·522, N_p 1·471.[523A]

The heat capacity, entropy, free-energy function, enthalpy and heat and free energy of formation of crystalline $K_2B_4O_7$ have been calculated[1085] from heat of solution data[750] and enthalpy data[783] and tabulated from 298 to 2000°K.[1085] The heat content of crystals in the K_2O–B_2O_3 system at a given temperature reaches a minimum at 20 mole-% K_2O.[783]

Differential thermal analysis of the crystalline diborate shows endothermic effects at 160°, 390° and 780°C.[523A] The amorphous compound has a strong exothermic peak at 510°C, attributed to crystallization.[523A]

Dipotassium tetraborate is rather hygroscopic.[451] When heated at 400°C in a current of humid air, it loses boric oxide slowly.[700] Deposited on porcelain or alumina, it is a catalyst in the oxidation of methane to formaldehyde using air or oxygen containing ozone or nitric oxide.[129A, 1224] Reaction rates and explosion limits for the hydrogen–oxygen reaction are reproducible when the vessel is coated with dipotassium tetraborate or potassium metaborate.[502A] The tetraborate is efficient in destroying chain carriers in this reaction.[892] Boron may be diffused into silicon by contacting the silicon with a suspension of dipotassium tetraborate in turpentine.[566]

POTASSIUM TRIBORATE, KB_3O_5 OR $K_2O,3B_2O_3$

The 1:3 compound, triclinic, *d* (calc.) 2·26[451], *d* (obs.) 2·23 g cm^{-3} [451], has an incongruent m.p. at 825°C.[698] It has been crystallized from a glass of the 1:4 composition.[451] Its *X*-ray diffraction pattern has been tabulated and its unit-cell data have been reported.[451]

The heat capacity, entropy, free-energy function, enthalpy, heat of formation and free energy of formation have been calculated and tabulated from 298 to 2000°K[1085] from published heat of solution measurements in nitric acid[750] and enthalpy determinations.[783]

DIPOTASSIUM OCTABORATE, $K_2B_8O_{13}$ OR $K_2O,4B_2O_3$

The 1:4 compound has a congruent melting-point at 857°C.[698] Its *X*-ray diffraction pattern has been tabulated and its infra-red absorption spectrum has been published.[444] Its heat capacity, entropy, free-energy function, heat content, heat of formation and free energy of formation have been calculated and extrapolated from published heat of solution measurements[750] and enthalpy determinations[780, 783] and tabulated from 298 to 2000°K.[1085] The heat of fusion is 30·16 kcal mole^{-1}.[780] Heat content in the system $K_2O,4B_2O_3$–$Na_2O,4B_2O_3$ has been determined at 25–1100°C.[783]

POTASSIUM PENTABORATE, KB_5O_8 OR $K_2O,5B_2O_3$

The 1:5 compound exists in three forms.[697] The α-form, orthorhombic, *d* (calc.) 1·86[444] or 1·93[458A], *d* (obs.) 1·95 g cm^{-3} [444], is stable from 720° to 780°C, its congruent melting point.[697] It changes to the β-form when heated at temperatures below 720°C. At 700° this change requires about 12 h if seed is present but as long as a month without seed.[697] When heated at temperatures below 690°C, the α-form changes to the γ-form.[697] *X*-Ray diffraction patterns[844], unit-cell data[444, 458A], and infra-red spectra[444] of the α-form have been reported. Its structure[458A] consists of two separate three-dimensional inter-penetrating networks, consisting of double-ring pentaborate groups like the boron–oxygen skeleton of the ion found in potassium pentaborate tetrahydrate, $KB_5O_8,4H_2O$.[933] These groups are joined to each other by sharing oxygen atoms. Groups sharing a common oxygen atom which is near a twofold screw-axis extend in opposite directions, resulting in less dense packing and a density lower than that of the β-form.

The β-form of the 1:5 compound, also orthorhombic[456], *d* (calc.) 2·24[456], or 2·29[458A], *d* (obs.) 2·15 g cm^{-3} [456], is stable between 500° and 720°C, and has been crystallized from melts containing as little as 5% of K_2O.[697] Its structure[455–6], consists of two separate interlocking three-dimensional boron–oxygen networks, consisting of pentaborate groups like those of the α-form, joined to each other by sharing oxygen atoms, to form helix chains connected to neighbouring chains. In the β-form a twofold screw-axis runs near the centre of the pentaborate groups, leading to denser packing and a density much higher than that of the α-form. The structure has been discussed in terms of the 'structon' theory.[1247] The β-form is isomorphous with β-$Rb_2O,5B_2O_3$.[420, 456, 694] Its *X*-ray diffraction pattern[844] and infra-red absorption spectrum[444] have been published. Its thermal analysis curve shows a horizontal portion at 760°C, attributed to metastable incongruent melting to form the 1:4 compound and a liquid.[697]

The γ-form, monoclinic[451, 840], *d* (calc.) 2·20[451], is the form usually produced when the amorphous product of dehydration of the octahydrate at 280°C is heated at 600°C in the absence of seed for two days.[697] Its unit-cell data have been reported.[451] It appears to be metastable at all temperatures.[697, 840] The metastable transition from γ- to β-form takes place at 690 ± 7°C[697]; the γ-form changes to the α-form above that temperature.

The infra-red absorption spectrum of an unspecified form of the 1:5 compound has been published.[899] It indicates the presence of boron atoms in both three- and four-coordination and is similar to the spectra of $Li_2O,5B_2O_3$ and $Rb_2O,5B_2O_3$.[899] The specific magnetic susceptibility of potassium pentaborate dehydrated at above 200°C was determined to be $-0{\cdot}394 \times 10^{-6}$ c.g.s. units.[663]

POTASSIUM ENNEABORATE, KB_9O_{14} OR $K_2O,9B_2O_3$

Since the 1:9 compound crystallizes very slowly at 440°C, some seeds of cæsium enneaborate, CsB_9O_{14}, were placed on the surface of potassium enneaborate glass to promote crystallization, and the glass was then heated for six weeks at 440°C to crystallize potassium enneaborate. Cæsium enneaborate promotes crystallization of the potassium compound, even though the *X*-ray diffraction patterns of KB_9O_{14}[844] and CsB_9O_{14} are not similar.[840] The heating curve of KB_9O_{14} has been interpreted to indicate a decomposition of the 1:9 compound at 560°C to give β-KB_5O_8 and a liquid containing 98·4 wt-% of boric oxide.[840] The heat content and entropy have been tabulated from 100° to 1100°C for KB_9O_{14} glass, and from 100° to 700°C after devitrifying for 72 h at 600°C.[783]

Chemical Reactions of the Anhydrous Potassium Borates

Anhydrous or hydrated alkali-metal borates react with methanol to give methoxyborates. *X*-Ray patterns of $KB(OCH_3)_4$ and $KB(OCH_3)_4,1{\cdot}5CH_3OH$ have been reported.[484]

$K_2O,2B_2O_3$ and $K_2O,5B_2O_3$ have been reported to react with liquid sulphur trioxide to give $K_2O,2B_2O_3,9SO_3$ and $K_2O,5B_2O_3,16SO_3$ respectively.[430] Later work indicated that a mixture of B_2O_3,SO_3, $K_2B_4O_2(SO_4)_5$ and $K_2B_2O(SO_4)_3$ were formed instead.[430A]

A study has been made of the distribution of boron in silicon produced by contacting single crystals of silicon with a suspension of $K_2B_4O_7$ in turpentine.[566]

Other reactions of the anhydrous potassium borates are referred to in the section on phase equilibria of the anhydrous borate systems, pp. 456–72.

HYDRATED RUBIDIUM BORATES

Phase Equilibria in the System Rb_2O–B_2O_3–H_2O

The 18°, 80° and 100°C isotherms in the Rb_2O–B_2O_3–H_2O system have been determined[706A, 840, 1204], except for the region having a very high alkali–metal oxide concentration. The 18° isotherm of the 1:1:2·5 compound as determined in the earlier work[706A] appears to be somewhat high; this has been attributed to the presence of carbon dioxide. At 18°C, the solid rubidium borate phases were compounds with the Rb_2O–B_2O_3–H_2O molar proportions 1:1:8, 1:1:2·5 (or 1:1:2·67), 1:2:5, and α-1:5:8.[840] At 80°C the 1:1:2·5 (or 1:1:2·67), 1:2:3, 1:2:5, 2:5:6, and α-1:5:8 compounds are in equilibrium with solutions.[840] At 100°C also, the 2:5:6 and α-1:5:8 compounds can exist in equilibrium with solutions, but if the 1:5:4 compound is used as a starting material, the β-1:5:8, 1:5:4 and 2:5:5 compounds are formed instead.[1204]

Tetrarubidium Diborate Hydrates, $Rb_4B_2O_5,nH_2O$ or $2Rb_2O,B_2O_3,nH_2O$

By analogy with the tetrapotassium diborates, a 2:1:*n* compound might be expected in the very alkaline region of the Rb_2O–B_2O_3–H_2O system, at temperatures above 100°C; however, no information on such a compound exists because this region has not been investigated.[840]

Rubidium Metaborate Hydrates

SOLUBILITY

Solubilities in the system $RbBO_2$–H_2O have been determined[840] and are listed in Table XVI.

Table XVI.—Solubility of Rubidium Metaborate in Water[840]

Temperature, °C	Solubility, wt-% $RbBO_2$	Solid phase data
−19	35 (estimated)	Ice and $RbBO_2,4H_2O$
−13·6	37·6	$RbBO_2,4H_2O$
0	44·4	
10	50·2	
18	57·45	
20	61·5	Transition
30	62·1	$RbBO_2,1{\cdot}25$ or $1{\cdot}33H_2O$
56	63·6	
80	66·7	

RUBIDIUM METABORATE TETRAHYDRATE, $RbBO_2,4H_2O$ OR $Rb_2O,B_2O_3,8H_2O$

The 1:1:8 compound crystallizes in orthorhombic prisms from its highly concentrated solutions at about −10°C[477] and has also been crystallized at room temperature by using seed crystals prepared at −80°C.[840] It did not appear in early work[706A], as it apparently does not crystallize at room temperature unless seed is present.[840] Solubility and heating-curve studies, however, have shown that it is the stable phase in contact with its solutions from −19° to +20°C.[840] Other authors reported that the crystals melt in their own water of crystallization at about 15°C.[477]

RUBIDIUM METABORATE 1¼- OR 1⅓-HYDRATE, $RbBO_2,1\frac{1}{4}$ OR $1\frac{1}{3}H_2O$

The 1:1:2·5 compound[840, 844], orthorhombic, *d* (*X*-ray) 2·97 g ml^{-1} [947] may actually be the 1:1:2⅔ compound.[477, 947] One analysis gave the 1:1:3 composition.[249] It is stable in contact with its solution from 20° to 190°C, where it decomposes to form the 1:1:0·5 (or 1:1:0·67) compound and a liquid containing about

79 wt-% of $RbBO_2$, according to heating-curve studies under pressure.[840] Its *X*-ray powder diffraction pattern has been published.[844] The approximate unit-cell parameters and the space-group have been reported.[947] This compound is isomorphous with the analogous potassium compound and forms solid solutions with it.[477] The infra-red spectrum indicates the presence of molecular water.[477]

Analysis of finely powdered crystals, dried over solid potassium hydroxide and phosphorus pentoxide to constant weight, gave the composition $RbBO_2,1{\cdot}33H_2O$.[477] When heated slowly, this material lost one molecule of water between 110° and 135°C, or between 130° and 145°C, depending on the particle size. The same water loss occurred when the crystals were heated at a constant temperature of 130°C for 9–10 h.[477] In another thermogravimetric study one molecule of water was given off between 140° and 195°C. The remaining water was largely lost between 217° and 250°C[840], and at 400°C the product was completely dehydrated. No amorphous stages appeared during the dehydration.[479] Another thermogravimetric curve has been published, indicating the loss of $\frac{1}{3}$ molecule of water below 210°C and substantially complete dehydration at 309°C.[947] DTA and DTGA curves show an endothermic effect with a maximum at about 240°C.[947]

RUBIDIUM METABORATE MONOHYDRATE, $RbBO_2,H_2O$ OR $Rb_2O,B_2O_3,2H_2O$

Experiments on the dehydration of products made by partially hydrating $Rb_2O,2B_2O_3$ with water vapour have been interpreted to indicate the possible existence of the 1:1:2 compound; however, *X*-ray diffraction patterns showed only a direct change from anhydrous Rb_2O,B_2O_3 to $Rb_2O,B_2O_3,2\frac{2}{3}H_2O$ during the hydration.[477]

RUBIDIUM METABORATE $\frac{1}{4}$- OR $\frac{1}{3}$-HYDRATE, $RbBO_2,\frac{1}{4}$ OR $\frac{1}{3}H_2O$

There is good evidence both for the 1:1:0·5[840, 844] and the 1:1:0·67[477, 479], composition. The *X*-ray diffraction pattern has been tabulated[844] and given as a diagram[477], indicating that this compound is isomorphous with the analogous potassium compound, with which it forms solid solutions.[477] The infra-red spectrum indicates the absence of molecular water.[477]

Heating curves under pressure have indicated that this compound is in equilibrium with its solution from 190° to 220°C[840], and that above 220°C the anhydrous salt is formed.[840]

The 1:1:0·67 compound, formed by slow heating of the 1:1:2·67 compound, became anhydrous between 160° and 175°C or between 170° and 200°C[477], depending on the particle size; in another study, it lost its water principally between 217° and 250°C.[840]

Dirubidium Tetraborate Hydrates

DIRUBIDIUM TETRABORATE PENTAHYDRATE, $Rb_2B_4O_7,5H_2O$ OR $Rb_2O,2B_2O_3,5H_2O$

The 1:2:5 compound is a stable phase in equilibrium with its solution from room temperature up to 104°C.[249, 840, 844] Its *X*-ray diffraction pattern[844] indicates that it is isomorphous with the analogous cæsium compound, but not with dipotassium tetraborate tetrahydrate, $K_2O,2B_2O_3,4H_2O$. The solubility is 19·4 wt-% $Rb_2O,2B_2O_3$ at 18°C[706A] and 60·1 wt-% $Rb_2O,2B_2O_3$ at 80°C.[840] Heating curves under pressure indicate a change to the 1:2:3 compound at 104°C, to the 1:2:2 compound at 172°C, to the 1:2:1 compound at 244°C and to anhydrous $Rb_2O,2B_2O_3$ at 320°C[840] in contact with $Rb_2O,2B_2O_3$ solution. A thermogravimetric curve of the 5-hydrate, carried out in air saturated at 90°C with water vapour, showed a loss of two molecules of water between 72° and 115°C, one between 145° and 190°C, one more between 245° and 315°C, and the last between 345° and 480°C.[840] There were plateaux at 115–145°, 190–245°, and 315–345°C, corresponding to the formation of the 1:2:3, 1:2:2, and 1:2:1 compounds, respectively.[840] A thermogravimetric study carried out in air saturated at 25°C with water vapour, showed only a single plateau between 118° and 150°C, corresponding to the formation of $Rb_2O,2B_2O_3,3H_2O$.[840] *In vacuo* all five molecules of water were lost between 35° and 200°C.[305]

DIRUBIDIUM TETRABORATE TRIHYDRATE, $Rb_2B_4O_7,3H_2O$ OR $Rb_2O,2B_2O_3,3H_2O$

The 1:2:3 compound is not hygroscopic, and may be kept at ordinary temperatures. Its *X*-ray diffraction pattern has been reported.[844] Its isotherm at 80°C[840] indicates that its solubility is incongruent at that temperature. Heating curves under pressure have indicated that it is in equilibrium with its own solution between 104° and 172°C.[840]

DIRUBIDIUM TETRABORATE DIHYDRATE, $Rb_2B_4O_7,2H_2O$ OR $Rb_2O,2B_2O_3,2H_2O$

The 1:2:2 compound, according to a study of heating curves under pressure, is in equilibrium with its solution from 172° to 244°C, where it decomposes to form the 1:2:1 compound in contact with its solution.[840] It also appeared in a thermogravimetric study of the 1:2:5 compound in air saturated with water vapour at 90°C. Under these conditions it was formed between 190° and 245°C.[840] Its *X*-ray diffraction pattern has been tabulated.[844]

DIRUBIDIUM TETRABORATE MONOHYDRATE, $Rb_2B_4O_7,H_2O$ OR $Rb_2O,2B_2O_3,H_2O$

Heating curves under pressure[840, 844] indicate that the 1:2:1 compound is in equilibrium with its solutions from 244° to 320°C. Under these conditions it decomposes at 320°C to form anhydrous $Rb_2O,2B_2O_3$ in contact with its saturated solution. In a thermogravimetric study of the 1:2:5 compound in air saturated with water vapour at 90°C, the 1:2:1 compound was present from 315° to 345°C.[840]

Tetrarubidium Decaborate Hydrates

TETRARUBIDIUM DECABORATE PENTAHYDRATE, $Rb_4B_{10}O_{17},5H_2O$ OR $2Rb_2O,5B_2O_3,5H_2O$

The 2:5:5 compound was formed in a study of the 100°C isotherm of the $Rb_2O–B_2O_3–H_2O$ system when the 1:5:4 compound was used as a starting material. Its thermogravimetric analysis gave plateaux at the 1:5:3 and 1:5:1 compositions.[1204]

TETRARUBIDIUM DECABORATE HEXAHYDRATE, $Rb_4B_{10}O_{17},6H_2O$ OR $2Rb_2O,5B_2O_3,6H_2O$

The 2:5:6 compound appeared in a study of the solubility isotherms in the system $Rb_2O–B_2O_3–H_2O$ at 80°C. Its *X*-ray diffraction pattern[844] does not resemble those of $2Na_2O,5B_2O_3,7H_2O$ or $2K_2O,5B_2O_3,5H_2O$.[840] Its congruent solubility at 80°C is 58·4 wt-% $2Rb_2O,5B_2O_3$.[840]

A thermogravimetric curve, beginning with wet crystals or with crystals dried at 80°C, showed that from 98° to 155°C the water content remained constant at the hexahydrate composition. Between 155° and 200°C, three molecules of water were lost; between 214° and 240°C, one more was given off and between 255° and 450°C, the remaining water was lost.[840] There were small plateaux at 200–214°C at the 2:5:3 composition, and at 240°–255°C at the 2:5:2 composition. The only similarity with the thermogravimetric curve of Auger's potassium borate, $2K_2O,5B_2O_3,5H_2O$, was the small plateau at the 2:5:3 composition. In a later study there were plateaux at the 2:5:3 and 2:5:1 compositions but not at 2:5:2.[1204]

Rubidium Pentaborate Hydrates

The α-1:5:8 compound, orthorhombic[693], has an *X*-ray pattern[844] analogous to that of the corresponding potassium salt, indicating that these two salts are isomorphous. One preparation had a composition between 1:5:7 and 1:5:8.[249] Heating curves under pressure have indicated that the 1:5:8 compound is converted into the 1:5:2 compound and a solution of about 55 wt-% $Rb_2O,5B_2O_3$ at about 166°C. Further heating under pressure forms the 1:5:1 compound at 262°C and the anhydrous pentaborate at 327°C in contact with saturated solutions.[840] The *X*-ray diffraction patterns of the 1:5:2 and 1:5:4 compounds have been reported.[844]

Solubility values for the pentaborate have been determined[700] and are listed in Table XVII. The boiling point of a saturated solution is 102·17°.[700]

Table XVII.—Solubility of RbB_5O_8 *in Water*[700]

(Solubilities are expressed as wt-% of RbB_5O_8;
the solid phase is α-$RbB_5O_8,4H_2O$)

Temperature, °C	Solubility	Temperature, °C	Solubility
−0·43*	1·57	45	5·75
0·2	1·58	60	8·69
5	1·72	70·4	11·5
13·4	2·21	82·4	15·2
18	2·57	88·15	17·75
30	3·58	102	23·75

* Cryohydric point

In thermogravimetric studies, dehydration of the α-1:5:8 compound was continuous without slowing at definite stages[840], but the β-1:5:8 compound gave large variations in the rate of dehydration.[1204] The 1:5:4 compound gave plateaux corresponding to the 1:5:4, 1:5:2 and 1:5:1 compounds.[1204] When heated *in vacuo*, the α-1:5:8 compound is stable up to 80°C, but there is a rapid loss of six molecules of water beginning at 100°C, and the last two molecules are lost between 120° and 320°C.[307]

Hydrated Double Borates of Rubidium

Dirubidium calcium octaborate dodecahydrate, $Rb_2O,CaO,4B_2O_3,12H_2O$, and *dirubidium strontium octaborate dodecahydrate*, $Rb_2O,SrO,4B_2O_3,12H_2O$ have been prepared, and their densities, *X*-ray diffraction, DTA, and optical properties have been studied.[284] Differential thermal analysis of the calcium compound showed that exothermic effects are accompanied by an increase in electrical conductivity. Two molecules of water were lost at 100–110°C, eight more up to 200°C, and the remaining two between 200° and 620°C.[303]

ANHYDROUS RUBIDIUM BORATES

Phase Equilibria in the System Rb_2O–B_2O_3

A study of the Rb_2O–B_2O_3 system from 27·1 to 90 wt-% B_2O_3, by means of heating curves, has indicated that compounds are formed with $Rb_2O:B_2O_3$ molar ratios 1:1 (two forms), 1:2, 1:3, 1:4, 1:5 (two forms), and 1:9.[694, 420] There are eutectics at 40% B_2O_3 (720°); 47·3% B_2O_3 (710°); 57% B_2O_3 (707°C); and a metastable eutectic at 57·5% B_2O_3 (700°C).[694] Rb_2O–B_2O_3 glasses containing more than 75% of B_2O_3 crystallize slowly and require reheating for about a week for complete crystallization.[694] Another study, regarded by the authors as a first approximation because of hygroscopicity and volatility, gave somewhat different melting points and provided optical and morphological characteristics of the phases.[213]

Crystalline Anhydrous Rubidium Borates

RUBIDIUM METABORATE, $RbBO_2$ OR Rb_2O,B_2O_3

The 1:1 compound crystallizes easily in long needles which become yellow at elevated temperatures. It exists in two forms. The *X*-ray diffraction powder pattern of the β-form has been tabulated, and indicates that the structure is rhombohedral and analogous to that of potassium metaborate.[844] Other patterns have been published.[213, 477] The β-form is stable below 695°C; as shown by heating curves and DTA, it changes reversibly at that temperature to the α-form.[420, 694] The α-form melts congruently at 860°C. It could not be cooled to room temperature without changing to the β-form, even by rapid quenching.[420, 422] Heat-capacity values from 12·8 to 313 K have been experimentally determined and other thermodynamic properties at 298·15 K have been calculated.[1073]

DIRUBIDIUM TETRABORATE, $Rb_2B_4O_7$ OR $Rb_2O,2B_2O_3$

The 1:2 compound, crystallizing in aggregates of fine needles, melts congruently at 725°C[694] or 713 ± 5°C.[80A] It has also been reported to crystallize as prismatic plates, m.p. 720°C.[213] Its *X*-ray diffraction pattern[80A, 844] resembles that of K_2O,-$2B_2O_3$[844], which is triclinic. Another published pattern, not in good agreement[213] may have been affected by volatility or water absorption from the air. The crystals are colourless when cold but yellow at high temperatures.[844]

TETRARUBIDIUM DECABORATE, $Rb_4B_{10}O_{17}$ OR $2Rb_2O,5B_2O_3$

The 2:5 compound is formed by heating the hexahydrate above 450°C[844], but it did not appear in studies of phase equilibria.[213, 422] Its *X*-ray diffraction pattern has been tabulated.[844]

RUBIDIUM TRIBORATE, RbB_3O_5 OR $Rb_2O,3B_2O_3$

The 1:3 compound, m.p. 750°C[694] or 760°C[213], is obtained in fine grains by reheating the glass for two or three days at 650°C. It has an *X*-ray diffraction pattern[422] resembling that of KB_3O_5, which is triclinic.[451] An orthorhombic structure has also been proposed.[213] Another *X*-ray powder pattern, not in agreement[213], may have been affected by volatility or water absorbed from the air. Refractive indices have been determined as N_g 1·548, N_p 1·508, $2V_0$ 65°.[213]

DIRUBIDIUM OCTABORATE, $Rb_2B_8O_{13}$ OR $Rb_2O,4B_2O_3$

The 1:4 compound crystallizes with difficulty, forming polyhedral crystals[422] or plates.[213] It melts incongruently at 735°C[420] to give α-$Rb_2O,5B_2O_3$ and a solution containing 59 wt-% of boric oxide.[420, 422, 694] Another m.p. given is 750°C.[213] *X*-Ray diffraction patterns have been tabulated[213, 422], which agree in some of the principal lines. Comparison of the pattern with that of the analogous potassium compound did not establish whether the two structures are similar.[422]

RUBIDIUM PENTABORATE, RbB_5O_8 OR $Rb_2O,5B_2O_3$

Like potassium pentaborate, rubidium pentaborate exists in three crystalline forms, one of which is metastable. Dehydration of the tetrahydrate at 350°C gives an amorphous product. Differential thermal analysis of this product gives an exothermic effect at 380°C, due to crystallization of the γ-form, which appears to be metastable at all temperatures.[420] The *X*-ray diffraction patterns of the γ-form[422] and of a product crystallized at 425°C[213], probably also the γ-form, have been tabulated. Because of the possibility of moisture absorption, data in the latter work[213] are regarded as approximate. A monoclinic structure has been suggested.[213] At about 500°C[420], 570°C[422], or 600°C[844] an irreversible change of the γ-form to the stable orthorhombic β-form[213] occurs.

The β-form is isomorphous with β-KB_5O_8.[420, 456, 694] Its *X*-ray diffraction pattern (samples crystallized between 600° and 660°C[844] and at 660°C[213]) has been tabulated. Its structure, like that of β-KB_5O_8, consists of two separate interlocking boron–oxygen networks comprising pentaborate groups joined to each other by sharing oxygen atoms to form helix chains, which are interconnected with neighbouring chains.[456] The pentaborate groups each consist of two perpendicular six-membered boron–oxygen rings sharing a tetrahedral boron atom.[933] The structure has been discussed in terms of the 'structon' theory.[1247] The infra-red spectra of β-RbB_5O_8 and β-KB_5O_8 are closely similar.[899]

When the β-form is heated, it changes reversibly at 633°C to the α-form, m.p. 775°C[694] or 785°C.[213] The α-form changed to other forms when cooled, even when quenched in liquid air.[420, 422] Samples heated several days at 400–700°C gave *X*-ray diffraction patterns of the β- and γ-forms.[420]

RUBIDIUM ENNEABORATE, RbB_9O_{14} OR $Rb_2O,9B_2O_3$

The 1:9 compound is stable below 572°C.[420] In heating-curve studies under pressure, it decomposed at that temperature to give β-$Rb_2O,5B_2O_3$ and a liquid containing 89·5 wt-% of boric oxide.[420] The *X*-ray diffraction pattern of the 1:9 compound has been reported.[422] In another investigation a different pattern was obtained which may have been affected by moisture.[213] The crystal system was said to be orthorhombic.[213] The refractive indices were N_g 1·557 and N_p 1·481.[213]

HYDRATED CÆSIUM BORATES

Phase Equilibria in the System Cs_2O–B_2O_3–H_2O

Solubility isotherms in the Cs_2O–B_2O_3–H_2O have been determined at −2°, 0°, 30°, 56° and 80° [420], 100° [1204, 420] and 18°C.[693, 706, 706A] The following Cs_2O:B_2O_3:-H_2O compounds are in equilibrium with solutions: 1:1:8 (two forms), 1:1:2, 1:2:5, 1:2:2, 2:5:7, and α-1:5:8. If the 1:5:4 compound is used as a starting material, the compounds β-1:5:8, 1:5:4, and 1:5:3 are formed rather than the α-1:5:8 compound.[1204] The 3:5:6, 1:3:4, 1:4:5, 1:5:4, and 1:12:11 compounds have been prepared by hydrolysis of trimethyl borate.[1237]

Cæsium Metaborate Hydrates

SOLUBILITY

Solubilities in the system Cs_2O,B_2O_3–H_2O have been determined[420] and are listed in Table XVIII. The α-1:1:8 compound melts incongruently at 83°C, and there is a eutectic, m.p. 78°C, at 76 wt-% $CsBO_2$ with solid phases α-$CsBO_2,4H_2O$ and $CsBO_2,H_2O$ [420, 422].

Table XVIII.—Solubilities in the System Cæsium Metaborate–Water[420]

Temperature, °C	wt-% $CsBO_2$	Solid phase	Temperature, °C	wt-% $CsBO_2$	Solid phase
−2	9·55	Ice	47	47·90	β-$CsBO_2,4H_2O$
−4	14·0		50	49·55	α- and β-$CsBO_2,4H_2O$
−5	17·5		56	51·00	α-$CsBO_2,4H_2O$
−6	21·0		64·5	54·45	
−7	24·0	Eutectic, ice–β-$CsBO_2,4H_2O$	70	57·20	
			78	61·00	
−5	24·60	β-$CsBO_2,4H_2O$	80	62·7	
−2	26·10		83	71·00	
0	27·75		78	76·00	α-$CsBO_2,4H_2O$ and $CsBO_2,H_2O$
3·5	28·20		100	76·55	$CsBO_2,H_2O$
6	29·20		110	77·70	
10	31·0				
15	33·4				
17·6	24·9				
20·6	36·2				
30	40·35				
35	42·35				

CÆSIUM METABORATE TETRAHYDRATE, α- AND β-$CsBO_2,4H_2O$ OR $Cs_2O,B_2O_3,8H_2O$

The β-1:1:8 compound, orthorhombic[706], crystallizes in large rectangular flakes.[477] It is the stable phase in contact with its solution from the cryohydric point, −7°C to 50°C, as indicated by solubility and thermal analysis.[420] Thermal-analysis studies have indicated that it changes reversibly to the α-1:1:8 compound at 50°C in the presence of its saturated solution, which contains 49·8 wt-% of $CsBO_2$.[420] The α-1:1:8 compound melts congruently at 83°C. Two somewhat different *X*-ray diffraction patterns of the β-1:1:8 compound have been reported.[422, 477] This compound was formerly regarded as the heptahydrate[249, 706, 706A], but more recent analyses of large crystals dried over saturated potassium hydroxide solution or washed with acetone and ether showed it to be the octahydrate.[477] This composition was confirmed by thermal analysis.[420]

Crystals of the β-1:1:8 compound effloresce in air. Over saturated potassium hydroxide solution, finely ground crystals reach a water content of 7·66 molecules in 20 days at room temperature.[477] Over phosphorus pentoxide or solid potassium hydroxide, the composition 1:1:2 is reached at room temperature in less than 100 days.[477] The same composition is reached by heating to 70°C at a rate of about 10° per hour. Further heating at this rate to about 120°C gave no further loss of water. The last two molecules were lost between 120° and 160°C.[477] Thermogravimetric analysis at 25°–50° per hour, in a current of nitrogen free of carbon dioxide, gave a water loss of six molecules between 60° and 150°C, and a plateau at the 1:1:2 composition between 150° and 240°C. The last two molecules of water are lost gradually at temperatures up to 350°C.[420] This behaviour suggests that six molecules of water exist as water molecules and two as hydroxyl groups; this conclusion is supported by infra-red studies.[477]

CÆSIUM METABORATE MONOHYDRATE, $CsBO_2,H_2O$ OR $Cs_2O,B_2O_3,2H_2O$

Thermal analysis under pressure and solubility determinations indicate that the 1:1:2 compound is stable in contact with its saturated solution from 78° to about 170°C, where it changes to an unidentified product.[420] Thus it may be crystallized by slowly evaporating a solution of the metaborate in an air stream free of carbon dioxide at 80°C, with seeding.[477] Two *X*-ray patterns, differing somewhat, have been published.[422, 477]

When a sample of the 1:1:2 compound, which had been made by dehydration of the 1:1:8 compound over phosphorus pentoxide, was heated at 5°C per hour, half its water was lost rapidly at about 160°C. An *X*-ray diffraction photograph of the resulting 1:1:1 composition showed a characteristic pattern plus a dark background indicating the presence of amorphous material. Above 300°C, another 30% of the water was lost. Complete dehydration was not reached until melting occurred at about 700°C.[477] At 209–500°C (composition 1:1:1 to 1:1:0·4) the principal lines of anhydrous cæsium metaborate were present. When the resulting material was heated at 650°C for 12 h, some cæsium oxide was lost, leaving an almost completely amorphous product with a $Cs_2O:B_2O_3$ molar ratio of 0·74:1.[477] If the 1:1:2 compound is heated rapidly to > 300°C, however, the water is completely lost without change in the $Cs_2O:B_2O_3$ ratio.[477]

Dicæsium Tetraborate Hydrates

SOLUBILITY

Solubilities in the $Cs_2B_4O_7$–H_2O system[420] are recorded in Table XIX.

Table XIX.—Solubility of Dicæsium Tetraborate in Water[420]

(Solubilities expressed as wt-% of $Cs_2B_4O_7$)

Temperature, °C	Solubility	Solid phase	Temperature, °C	Solubility	Solid phase
20	49·90	$Cs_2B_4O_7,5H_2O$	100	73·25	$Cs_2B_4O_7,5H_2O$
30	52·70		106	75·70	
47	57·75		110	77·0	
56	60·40		111	78·0	(Transition)
70	63·00		162	79·0	$Cs_2B_4O_7,2H_2O$
80	67·57		204	82·0	

DICÆSIUM TETRABORATE PENTAHYDRATE, $Cs_2B_4O_7,5H_2O$ OR $Cs_2O,2B_2O_3,5H_2O$

The 1:2:5 compound, orthorhombic[706], is isomorphous with the analogous rubidium compound.[422] Its *X*-ray diffraction pattern has been reported.[422] It exists in equilibrium with solutions in the ternary system at temperatures as low as −8·5°C, but its solubility is congruent only above 19°C.[420] Thermal-analysis studies under pressure have indicated that it decomposes at 111°C, in contact with its saturated solution (78 wt-% $Cs_2B_4O_7$), to form the dihydrate.[420]

In thermogravimetric studies at heating rates of 50°C per hour, the pentahydrate was stable at temperatures up to 105°C. Three molecules of water were lost between 105° and 165°C. The composition remained constant at $Cs_2B_4O_7,2H_2O$ between 165° and 230°C. The last two molecules of water were lost between 230° and 400°C.[420] When heated *in vacuo*, the 1:2:5 compound was stable up to 70°C and then lost three molecules of water rapidly; the last two molecules were lost gradually as the temperature was increased to 400°C.[307]

DICÆSIUM TETRABORATE DIHYDRATE, $Cs_2B_4O_7,2H_2O$ OR $Cs_2O,2B_2O_3,2H_2O$

The 1:2:2 compound is stable in equilibrium with liquids in the ternary system $Cs_2O–B_2O_3–H_2O$ at temperatures as low as 76°C[420]; but in contact with its own saturated solution under pressure, it is stable only between 111° and 230°C.[422] Thermal-analysis studies under pressure have indicated that it is converted to the anhydrous salt at 230°C in contact with a saturated solution containing 82 wt-% of $Cs_2O,2B_2O_3$.[420] The *X*-ray diffraction pattern of the 1:2:2 compound has been tabulated.[422] In thermogravimetric studies, it was stable at temperatures up to 230°C and lost its water between 230° and 400°C.[420]

Tetracæsium Decaborate Hydrates

The 2:5:7 compound, $Cs_4B_{10}O_{17},7H_2O$ (or $2Cs_2O,5B_2O_3,7H_2O$), is stable in contact with solutions in the $Cs_2O–B_2O_3–H_2O$ system at temperatures as low as 45°C, but its solubility is congruent only above about 78°C.[420] Its *X*-ray diffraction pattern has been tabulated.[422] The solubility isotherms[420] indicate a congruent solubility of about 56% wt-% of $2Cs_2O,5B_2O_3$, at 80°C and about 59% at 100°C.

A thermogravimetric curve[420] showed that the 2:5:7 compound is stable up to 110°C. Between 110° and 150°C, four of the seven molecules of water were lost, and between 150° and 280°C, the composition remained constant at three molecules of water. Dehydration is practically complete at 500°C.[420]

Cæsium Pentaborate Hydrates

SOLUBILITY

Values in the system $CsB_5O_8–H_2O$[700] are listed in Table XX.

Table XX.—Solubility of Cæsium Pentaborate in Water[700, 420]

(The solid phase throughout is $CsB_5O_8,4H_2O$, −0·36°C being its eutectic with ice; solubilities are expressed as wt-% CsB_5O_8)

Temperature, °C	Solubility	Temperature, °C	Solubility
−0·36	1·59	93	19·5
5	1·68	93·6	19·75
18	2·33	95	20·4
30	3·52	99·1	22·3
45	5·57	99·5	22·6
60	8·31	101·65	23·45
75	12·0	127	38*
80	13·8	150	50*
89·4	17·85	162	57*

* Determined by thermal analysis under pressure[420]

CÆSIUM PENTABORATE TETRAHYDRATE AND MONOHYDRATE, $CsB_5O_8,4H_2O$ AND H_2O OR $Cs_2O,5B_2O_3,8H_2O$ AND $2H_2O$

The α-1:5:8 compound, orthorhombic[693], is stable in contact with its saturated solution from −0·36° (cryohydric point) to 162°C. It was formerly believed to be the 1:5:7 compound.[249] Its *X*-ray diffraction pattern has been tabulated.[422] Thermal analysis studies under pressure have been interpreted to indicate that it decomposes at 162°C to form the 1:5:2 compound and a saturated solution containing 57 wt-% of CsB_5O_8.[420] In later work, it was converted into the 1:5:4 compound when heated in a sealed tube to 200°C.[1204] In thermogravimetric studies, it dehydrated continuously without slowing at definite stages.[1204] The dehydration rate became slower as the water content decreased below two molecules, and the anhydrous state was reached at about 450°C.[307, 420] The β-1:5:8 compound, however, shows variations in the rate of dehydration. The 1:5:4 compound shows plateaux at the 1:5:4, 1:5:3, 1:5:2, and 1:5:1 compositions.[1204] *In vacuo* six of the eight molecules of water were lost rapidly between 70° and 115°C, and the last two were lost gradually between 115° and 400°C.[307]

Hydrated Double Borates of Cæsium

Dicæsium calcium octaborate dodecahydrate, $Cs_2O,CaO,4B_2O_3,12H_2O$, and *dicæsium strontium octaborate dodecahydrate*, $Cs_2O,SrO,4B_2O_3,12H_2O$, have been prepared, and their densities, *X*-ray, DTA, and optical properties have been studied.[284] When the calcium compound is heated, exothermic effects are accompanied by an increase in electrical conductivity. It loses two molecules of water at 100°–110°C, eight more at 200°C, and the last two between 200° and 620°C.[303]

ANHYDROUS CÆSIUM BORATES

Phase Equilibrium in the System $Cs_2O–B_2O_3$

Studies of the $Cs_2O–B_2O_3$ system from 20 to 80 wt-% B_2O_3 by the heating-curve method showed that compounds with the $Cs_2O:B_2O_3$ molar ratios 1:1, 1:2, 1:3, 1:4, 1:5 (three forms) and 1:9 (two forms) exist.[418, 420, 454] There are eutectics at 29·9 wt-% B_2O_3 (622°C), 53·5% (662°C), and 66·0% (591°C). If the 1:4 compound does not crystallize, a metastable eutectic occurs at 645°C, consisting of the 1:3 and 1:5 compounds.[420] Mixtures rich in boric oxide are difficult to crystallize.[420]

Crystalline Anhydrous Cæsium Borates

CÆSIUM METABORATE, $CsBO_2$ OR Cs_2O,B_2O_3

The 1:1 compound crystallizes readily in long needles, which change from white to yellow when heated and melt at 732°C[418] to form a red-brown liquid. Two different *X*-ray diffraction patterns have been tabulated[422, 477], one of which[422] indicated that the structure is simple cubic, with $a = 6·82$ Å.

DICÆSIUM TETRABORATE, $Cs_2B_4O_7$ OR $Cs_2O,2B_2O_3$

The 1:2 compound crystallizes in tufts of long needles and changes from white to yellow when heated. At 691°C, it decomposes to form the triborate and a liquid containing 31·5 wt-% of B_2O_3.[418] Its *X*-ray diffraction pattern has been reported.[422]

CÆSIUM TRIBORATE, CsB_3O_5 OR $Cs_2O,3B_2O_3$

The 1:3 compound, orthorhombic[418, 422, 454], *d* (calc.) 3·39[454], melts congruently at 842°C. Its *X*-ray diffraction pattern has been tabulated[422], and its infra-red absorption spectrum reported.[899] The structure[459] is based on triborate groups, which are six-membered rings of alternate boron and oxygen atoms, one of the boron atoms of the ring having four-fold and the other two having three-fold coordination with oxygen. The oxygen atoms not in the rings are shared between the triborate groups to give a continuous three-dimensional network. The structure has been discussed in terms of the 'structon' theory.[1247]

DICÆSIUM OCTABORATE, $Cs_2B_8O_{13}$ OR $Cs_2O,4B_2O_3$

The 1:4 compound, pseudocubic with $a = 5{\cdot}74$ Å[454], melts incongruently at 672°C with formation of the 1:3 compound and a liquid containing 50·4 wt-% of B_2O_3. It is birefringent.[454] Its *X*-ray diffraction pattern has been tabulated.[422]

CÆSIUM PENTABORATES, α-, β-, AND γ-CsB_5O_8 OR $Cs_2O,5B_2O_3$

Thermal analysis and *X*-ray diffraction patterns[422] have indicated that the 1:5 compound exists in three different forms. The γ-form, obtained by dehydration of the tetrahydrate at 400°C, changes to the β-form at 570°C.[420, 422] The β-form changes to the monoclinic[454] α-form at 640°C.[420, 422] The density of the α-form is 3·0, (obs.), 3·04 (calc.) and its unit-cell data have been determined.[454] Its congruent melting point is 669°C.[420] A precipitate, made by mixing alcoholic solutions of cæsium oxide and boric acid with five or more molecules of boric oxide per molecule of cæsium oxide, has the 1:5 composition and appears to be amorphous.[706]

CÆSIUM ENNEABORATES, α- AND β-CsB_9O_{14} OR $Cs_2O,9B_2O_3$

The 1:9 compound exists in two forms, of which the *X*-ray powder diffraction patterns have been tabulated.[422] The β-form, monoclinic, m.p. 562°C, is metastable and occurs as a fine white powder. At some temperature between 510° and 570°C, it recrystallizes to the α-form.[454] Approximate unit-cell constants have been reported for the β-form; its density is estimated to be about 2·6.[454]

The α-form, congruent m.p. 596°, *d* (obs.) 2·47, *d* (calc.) 2·51, pseudotetragonal[457], is stable and occurs as small translucent polyhedra.[420] The structure of the α-form[457] is made up of two separate interpenetrating networks of boron and oxygen atoms. The networks consist of 'boroxol' groups and triborate groups in the ratio of 2:1, connected by shared oxygen atoms.[457] The 'boroxol' group is a six-membered ring of alternate boron and oxygen. The triborate group is the same except that one of the boron atoms is tetrahedrally coordinated with oxygen.[457] The structure has been discussed in terms of the 'structon' theory.[1247]

The infra-red spectrum of the 1:9 compound has been published.[899]

AQUEOUS SOLUTIONS OF ALKALI–METAL BORATES

Physical Properties

DISSOCIATION

Monoborate Ion

In aqueous solutions of alkali–metal metaborates, MBO_2, the borate exists as the monoborate ion, $B(OH)_4^-$, which is tetrahedral and monomeric. Cryoscopic studies of sodium metaborate in the eutectic of sodium sulphate decahydrate[215] and in molten calcium chloride hexahydrate[519] and nuclear magnetic resonance studies[579], show that sodium metaborate is a binary electrolyte. The freezing-point lowering in aqueous solutions containing up to 13% of $NaBO_2$ is similar to that of potassium bicarbonate, a binary electrolyte[560], indicating that little, if any, polyion formation occurs in these solutions. The tetrahedral structure of the ion is indicated by studies of Raman and infra-red spectra. The number and positions of the Raman lines of 10N potassium metaborate solution do not agree with the BO_2^- or $H_2BO_3^-$ structures.[229] The Raman spectrum is similar to that of $NaBF_4$ solutions and corresponds with the infra-red spectrum of teepleite, $NaB(OH)_4,NaCl$ which contains tetrahedral $B(OH)_4^-$ions[257–8], thus confirming that the monoborate ion is tetrahedral.[229]

Polyborate Ions

Boric acid in dilute solution is also monomeric. However, in mixtures of metaborate and boric acid solutions, the ions are polymerized to a relatively large extent unless the solutions are very dilute. The polyions can be considered to be formed by elimination of water between boric acid molecules, $B(OH)_3$, and the monoborate ions, $B(OH)_4^-$. Evidence for polymerization can be found in data on the solubility of the alkali–metal borates, heat of neutralization, distribution equilibria, freezing points, pH values, infra-red and Raman spectra, n.m.r., conductivity and ion-exchange studies[237], as discussed in the following sections. Measurements of pH have indicated that polyboric acids depolymerize rapidly when the solution is diluted, the half-life being less than 10 s.[230A] Oxygen-isotope studies have indicated that the interchange of heavy oxygen between borax and water reaches equilibrium in less than a few minutes[921], or less than 4 h.[310] Boron exchange among ions is too rapid to be detected by nuclear magnetic resonance.[341, 579, 627] The rate constants for the formation of the $[B_3O_3(OH)_4]^-$ ion from $B(OH)_4^-$ and $2B(OH)_3$ and for the formation of $[B_5O_6(OH)_4]^-$ from $[B_3O_3(OH)_4]^-$ and $2B(OH)_3$, have been evaluated from relaxation times measured by the temperature-jump method.[17] The rate constants for the formation of boric acid and hydroxide from the metaborate ion were evaluated by means of ultrasonic absorption measurements.[926]

Evidence for Polyborate Ions from Solubility

When borax is added to a saturated boric acid solution, or boric acid to a saturated borax solution, the solubility, measured by the percentage of boric oxide in solution, increased (Fig. 1). This increase can be explained by formation of polyborate ions, which removes from the solution some of the boric acid molecules and borate ions which are in equilibrium with the solids, and thus allows more borax or boric acid to dissolve. The same behaviour occurs with the other alkali borates.[682]

In solutions saturated with boric acid containing up to about 0·18 molecule of Na_2O per mole of B_2O_3, the pH is less than 7.[863A] The ratio of free monoborate ion concentration to free boric acid concentration must therefore be small, according to the equation $[B(OH)_4]^-/[H_3BO_3] = 6 \times 10^{-10}/[H^+]$. The concentration of free boric acid in these solutions, except for activity considerations, should be equal to the solubility of boric acid in water. The amount of boric oxide present in excess of this amount should therefore exist in the form of polyborate ions. An early calculation from the solubility of boric acid in borax solution showed that the polyborate ions in this region contained on the average four to five atoms of boron per univalent negative ion.[35] More recent conductivity and freezing-point data[389, 808] indicate that the complex is probably pentaborate in solutions containing 3% of boric acid. A review of work on the nature of the ions in borate solutions was made in 1962, and a mathematical study has been carried out which gives an approximate representation of the constitution of various idealized borate solutions at room temperature[1167], assuming that $[B_3O_3(OH)_4]^-$ is the only polyion formed.

THERMAL PROPERTIES

The heat of neutralization of one mole of sodium hydroxide (dilution about 300–400 moles of water per mole of alkali) with boric acid solution has been found to be, with one mole of boric acid, 10,010 g cal; with two moles of boric acid, 11,100 g cal; four moles, 12,800 g cal; and with six moles of boric acid, 13,600 g cal. This indicates that complex formation occurs and that it is an exothermic process.[562]

The specific heat of borax solutions decreases with increased concentration up to 20% $Na_2B_4O_7$ and increases between 24 and 29°.[737] Experimental values are:

$Na_2B_4O_7$, wt-%	1	2·5	3·8	5·0	10·0	12·0	14·0	16·0	20·0	24·0	29·0
Specific heat, g cal g^{-1}	0·987	0·975	0·965	0·956	0·918	0·903	0·887	0·872	0·842	0·854	0·880

Another study[646], at 18–20°C, gave:

$Na_2B_4O_7,10H_2O$, g per 100 g H_2O	1	2	3	4	4·5
Specific heat, g cal g^{-1}	0·992	0·984	0·976	0·970	0·966

The heat of formation of sodium metaborate dissolved in 300 moles of water was evaluated as $-241{\cdot}1$ kcal mole^{-1}.[1118]

From an experimental study of the volatility of borate from boric acid and potassium and lithium tetraborate solutions (molar ratio K_2O/B_2O_3 or Li_2O/B_2O_3 approximately 0·5) at 100°–300°C, the stability constant of $[B_3O_3(OH)_4]^-$ in this temperature range was evaluated. This permitted an estimation of the amount of boron in various species at these temperatures.[1167]

DISTRIBUTION EQUILIBRIA WITH ALCOHOLS

Since boric acid is soluble in amyl alcohol, but borate ions are not, it is possible to determine the concentration of free boric acid in borax solutions by distribution experiments. In 1·9, 3·8 and 7·85% borax solutions the free boric acid concentration was 86·4, 58·7 and 32·2%, respectively, of what it would be if the borax were completely dissociated to monoborate and free boric acid.[587] Distribution experiments using octyl alcohol with solutions having various ratios of Na_2O/B_2O_3 indicated that polyborate ions are formed.[55] A solution of 9·5 g of borax per litre contains 2·5 g of free boric acid, and a solution of 24·8 g of borax per litre, 3·4 g of free boric acid.[787] These amounts are respectively 72% and 42% of the boric acid concentrations which would be expected if no polyions were present. Distribution experiments with isoamyl alcohol indicated that in sodium metaborate, borax or sodium pentaborate solutions containing 0·07% of boric oxide, only a small proportion of the borate ions are polyions.[806] The polyions were thought to be different when different cations were present.[389, 808, 813] Studies have been made of the distribution of boric acid between octanol-1 and various Na_2O–B_2O_3–$NaClO_4$ solutions saturated with borax and K_2O–B_2O_3-KCl solutions saturated with potassium pentaborate, $KB_5O_8,4H_2O$.[56]

CRYOSCOPY

Freezing points of lithium, sodium, and potassium metaborate solutions have indicated binary dissociation.[560, 562] Freezing points of tetraborate solutions ($Li_2B_4O_7$, $Na_2B_4O_7$ and $K_2B_4O_7$) have been interpreted as indicating a preponderant dissociation into BO_2^- and free boric acid in dilute solutions, and probably the formation of $B_4O_7^{2-}$ to a large extent in concentrated solutions.[562] Cryoscopic results on pentaborate solutions (LiB_5O_8, NaB_5O_8 and KB_5O_8) have indicated almost complete dissociation of pentaborate into monoborate and free boric acid in very dilute solutions; in 0·3M pentaborate solutions, the results suggest that about half of the borate present exists as monovalent pentaborate ions. Data on still more acidic solutions suggest a considerable dissociation of pentaborate at a B_2O_3/Na_2O molar ratio of 14.[562]

Freezing points of borax solutions, extrapolated to infinite dilution, indicate three particles per sodium ion.[215, 562] In very dilute solutions borax must then be largely dissociated into monoborate ion and free unionized boric acid. In 3·8% borax solution, however, the freezing-point data indicate 1·9 particles per sodium ion, indicating polyion formation.[376] At higher concentrations the freezing-point lowering of dipotassium tetraborate ($K_2B_4O_7$) approaches that of sodium sulphate, potassium sulphate and potassium carbonate. At 0·5M $K_2B_4O_7$ the apparent number of particles per molecule is 2·19 compared with 2·25 for potassium sulphite, suggesting that the $B_4O_7^{2-}$ ion is present at this concentration.[562] Other cryoscopic studies with alkali-metal metaborates, tetraborates and pentaborates also indicate dissociation to $B(OH)_4^-$ and $B(OH)_3$ in dilute solutions.[389]

The freezing points of a series of solutions between $B(OH)_3$ and $B(OH)_4^-$ having the same total boron content have been determined.[787] The number of boron-containing particles per boron atom was one in boric acid solutions and in sodium metaborate solutions, but was less in mixtures of the two. In solutions containing 9 g of boric oxide per litre, a minimum corresponding to 0·7 particle per atom of boron occurred at a molar ratio $Na_2O/B_2O_3 = 0{\cdot}4$. Polymerization therefore appears to be at a maximum at this molar ratio, which corresponds to the isohydric point (see

p. 414). In another study, which included freezing points, pH measurements, and distribution of boric acid between borate solutions and octyl alcohol, it was concluded that HBO_2, BO_2^-, $B_4O_7^{2-}$ and $B_5O_8^-$ were present, and the proportions of each were calculated.[513]

In fused hydrated sodium thiosulphate, cryoscopy studies indicated that the apparent molecular weight of disodium tetraborate was 140, rather than the formula weight, 201·27.[111] Cryoscopic studies of sodium metaborate and borax in the eutectic of sodium sulphate decahydrate indicated that the metaborate formed one particle and borax formed four.[215] The lowering of the melting point of $CaCl_2,6H_2O$ by lithium metaborate indicated binary dissociation.[519] Activity coefficients for disodium and dipotassium tetraborates and sodium metaborate were evaluated from the freezing points of their solutions.[650A]

pH VALUES

Since borax in dilute solution is largely dissociated into free boric acid molecules and an equal number of monoborate ions, it is an excellent buffer and a 0·01M solution (3·81 g $Na_2B_4O_7,10H_2O$ per litre) has been recommended as a pH standard by the National Bureau of Standards.[525] The pH values of a 0·01M borax solution, assigned by the National Bureau of Standards are as follows[113, 1078A]:

Temperature, °C	0	5	10	15	20	25	30	35	40
pH	9·46	9·39	9·33	9·27	9·22	9·18	9·14	9·10	9·07
Temperature, °C	45	50	55	60	70	80	90	95	
pH	9·04	9·01	8·99	8·96	8·93	8·89	8·85	8·83	

Precise values have been determined with cells with liquid junctions using hydrogen and saturated calomel electrodes, for freshly prepared borax solutions, as follows[1189A]:

Temperature, °C	0	10	20	25	30	40	50	60
0·01M Borax	9·454	9·330	9·228	9·185	9·144	9·076	9·020	8·975
0·05M Borax	9·479	9·347	9·326	9·183	9·142	9·056	8·994	8·943

There was a decrease of 0·001 to 0·002 pH unit when these borax solutions were allowed to stand for several hours.[1189A] The pH of the 0·01M solution is decreased by 0·001 unit when 0·2% of carbon dioxide is absorbed.[1078A] pH values have been measured at 30°C and 60°C in the aqueous systems $NaOH–H_2BO_3$, $Na_2B_4O_7–H_3BO_3$, $Na_3PO_4–H_3BO_3$, $Na_2HPO_4–H_3BO_3$, $Na_2CO_3–H_3BO_3$, $Na_2B_4O_7–NaHCO_3$, $Na_2B_4O_7–Na_2CO_3$, $Na_2B_4O_7–Na_2HPO_4$, $Na_2B_4O_7–Na_3PO_4$.[402] The values for the first two systems are given in Tables XXI and XXII. Essentially the same results were obtained in borax and in sodium metaborate solutions, 0·05–0·15N, by other investigators.[548]

The composition of borax–hydrochloric acid solutions giving pH values from 8·0 to 9·1, and borax–sodium hydroxide solutions giving pH values from 9·2 to 10·8, at 0·1 intervals, have been published, with information on the effect of temperature change, alkali addition and dilution on the pH value.[57] Air-stable standards covering the range of pH from 7·8 to 11·65 are prepared by aeration of 0·05M-H_3BO_3–0·05M-HCl–NaOH solutions for 2 to 6 days. Stable buffers more alkaline than pH 9·4 cannot be prepared.[245]

In other work, the pH of sodium borate solutions was determined at 20°C at 0·01–0·1M-H_3BO_3 and 0–0·4M-NaOH[260], and pH values for $2NaCl–Na_2B_4O_7$ solutions at ionic strengths 0·01–0·05 from 0° to 60°C have been determined in cells without liquid junctions.[524] Similar studies were made in which the concentrations of borax and sodium chloride were varied.[525]

An 'acidity function' useful for measuring the acidic or basic character of electro-

Table XXI.—pH Values of $NaOH$–H_3BO_3 *Solutions at 30°C*[402]

(Values at 60°C are given in parentheses)

Moles H_3BO_3 per litre	Moles NaOH/litre						
	0	0·05	0·1	0·2	0·3	0·4	0·5
0		12·36	12·64	12·90	13·03	13·16	13·24
0·05	5·83 (6·18)	10·43	12·33	12·83	13·00	13·12	13·22
0·1	5·43	9·12	10·68	12·64	12·87	13·04	13·13
0·2	4·83	8·47	9·12 (8·94)	11·01	12·64	12·91	13·07
0·3	4·70	8·00	8·67	9·56	11·28	12·61	12·96
0·4	4·62	7·60	8·30	9·18	9·90 (9·63)	11·38	12·65
0·5	4·17	7·25	7·95	8·88	9·50	10·05	11·39 (10·88)

Table XXII.—pH Values of $Na_2B_4O_7$–H_3BO_3 *Solutions at 30°C*[402]

(Values at 60°C are given in parentheses)

Moles H_3BO_3 per litre	Moles $Na_2B_4O_7$/litre						
	0	0·025	0·05	0·075	0·1	0·125	0·15
0		9·16	9·15	9·19	9·18	9·23	9·21
0·05	5·83 (6·18)	8·75	8·89	8·96	9·01	9·05	9·09
0·1	5·43	8·47	8·68	8·78 (8·62)	8·86	8·91	8·95
0·2	4·83	8·00	8·30	8·46	8·56	8·65 (8·44)	8·72
0·3	4·70	7·60	7·95	8·16	8·29	8·41	8·49 (8·31)
0·4	4·62	7·24	7·60 (7·53)	7·88	8·03	8·17	8·28
0·5	4·17	6·94	7·34	7·60	7·80	7·94	8·07

lytic solutions was discussed and determined in borax–sodium chloride solutions at temperatures from 0° to 60°C.[58]

The pH values of various saturated solutions in the Na_2O–B_2O_3–H_2O and K_2O–B_2O_3–H_2O systems at 25°C have been determined.[863A] In the Na_2O–B_2O_3–H_2O system the pH values at 18°C of solutions containing 0·94, 1, 2, 3, 4·3, 5 and 6 moles of boric oxide per mole of sodium oxide, diluted with various amounts of water up to 1400 l mole^{-1}, were also given. As these solutions were diluted to 1000 l mole^{-1}, the pH approached values between 8·4 and 9·1. In this work a solution with three moles of boric oxide per mole of sodium oxide changed its pH very little, from 8·73 to 8·78, on diluting from 10 to 1000 l mole^{-1}.[863A]

The pH of potassium metaborate solutions has been determined at 20°C as follows[1117A]:

KBO_2, wt-%	0·1	1·0	5·0	10·0	20·0	30·0	42·9
pH at 20°C	10·58	11·19	11·78	12·22	12·98	13·72	14·91

When a solution containing 0·08 mole of boric acid and 0·05 mole of borax per litre was diluted to ten times its volume with slightly acidified water having a pH of 5·2 at 16·2°C, the pH remained constant at 8·68. Dilution with pH 5·2 water to

100 volumes decreased the pH to 7·53; to 200 volumes, 6·84; to 333 volumes, 6·35; to 500 volumes, 6·05; and to 1000 volumes, 5·70.[878]

pH values have been measured[429] for mixtures of *b* ml of borax solution (19·10 g of $Na_2B_4O_7,10H_2O$ per litre) and $(100-b)$ ml of sodium carbonate solution (5·3 g of Na_2CO_3 per litre) as follows:

b	2·7	5·25	8·5	13·1	17·85	24·6	33·3	44·5	64·3	100·0
pH	11·00	10·80	10·60	10·40	10·20	10·00	9·80	9·60	9·40	9·20

The pH values of 0·01M solutions of borax in water and in 10, 20 and 40% solutions of methanol in water have been determined.[654]

Curves have been published showing the effect of cetomacrogol, a nonionic surfactant, on the pH of a borax solution.[214]

The pH of a borax solution changes very little with dilution and the pH of a solution having a Na_2O/B_2O_3 molar ratio of 0·412 remains constant at 8·91 when the solution is diluted.[548] However, if an alkali-metal borate solution has a pH value much higher or lower than these values, its pH will change appreciably with the concentration. Solutions which are more acidic than these solutions become still more acidic at higher concentrations, and solutions more alkaline than this become still more alkaline. This behaviour can be explained qualitatively by the formation of polyborate ions.[428] When a polyborate solution is diluted, the ions rapidly reach a new equilibrium in which more boric acid molecules and monoborate ions are formed. If this dissociation produces boric acid and monoborate ions in a ratio less than the ratio $[H_3BO_3]/[B(OH)_4^-]$ in the original solution, the effect of dilution will be to decrease this ratio and thus increase the pH. Similarly, if the ratio $[H_3BO_3]/[B(OH)_4^-]$ in the original solution is less than the ratio formed by dissociation of the polyborate ions, the effect of dilution will be to decrease the pH. If the $[H_3BO_3]/[B(OH)_4^-]$ ratio in the original solution is the same as that formed by dissociation of the polyborate ions, the pH will be independent of the dilution. In experiments on the pH during titration of boric acid with hydroxide at various concentrations this composition was found and called the isohydric point.[141–3, 144A, 1225–6, 788–9] In the titration of boric acid with potassium hydroxide the isohydric point is at a K_2O/B_2O_3 molar ratio of 0·405 and pH = 9·00; in the presence of 2M-KCl it is at molar ratio 0·397 and pH 8·74. In the sodium borate system at 30°C at concentrations 0·005–0·15N, it is at a Na_2O/B_2O_3 molar ratio of 0·412 and pH = 8·91.[548] The $B(OH)_4^-$ ions and the $B(OH)_3$ molecules are therefore removed from solution in a molar ratio close to 2:3. If a single polyborate ion were to be formed it would then be the divalent pentaborate ion $[B_5O_6(OH)_5]^{2-}$. This ion is found in crystalline tetravalent decaborates. It has been thought that this polyion is the only one formed in borate solutions[143, 144A, 1226] but other interpretations indicate the presence of $B_5O_8^-$ and $B_4O_7^{2-}$ [786, 788]; HBO_2, $HB_2O_4^-$ and $B_5O_8^-$ [145]; $HB_2O_4^-$, $B_4O_7^{2-}$, $HB_4O_7^-$ [476, 476A]; $B_5O_8^-$ [476]; and $B_3O_3(OH)_5^{2-}$ and $B_3O_3(OH)_4^-$.[1115A] Experiments on the lowering of the transition point of sodium sulphate, pH titrations and distribution of boric acid between solutions and octyl alcohol have indicated that HBO_2, BO_2^-, $B_4O_7^{2-}$ and $B_5O_8^-$ are present; their proportions were calculated.[513] Theoretical studies[137] have indicated that probably two groups of ions predominate at the isohydric point, each group containing ions having a similar degree of polymerization. These studies also indicated that maximum polymerization occurs at the isohydric point. In the titration of boric acid–metavanadate, boric acid–dichromate and boric acid–tartaric acid mixtures with sodium hydroxide, the isohydric point coincided with the minimum freezing-point lowering.[789]

Ingri *et al.*[353–4, 354A, 355–6] reviewed previous work on borate structures and the nature of borate solutions, and made pH titrations of boric acid (at concentrations up to 0·6M) with sodium hydroxide in 3M sodium chlorate, obtaining a set of curves. The data were analyzed mathematically. The results confirmed that in solutions more dilute than about 0·1% B_2O_3 the borate species present are essentially only

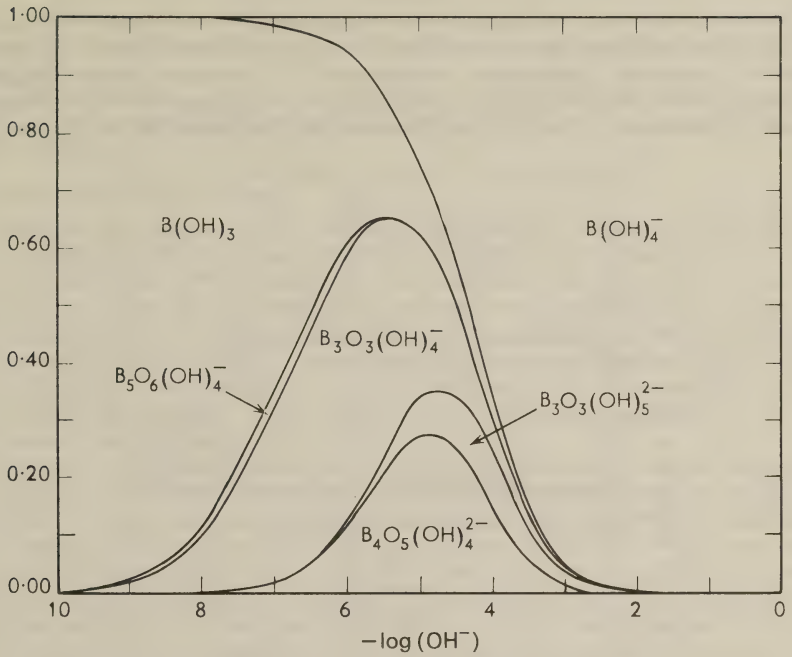

FIG. 12.—Distribution of boron between different ions at 25°C.[353] At a given log $[OH^-]$ the fraction of boron, α, present as a given ion, is represented by the segment of a vertical line falling within the corresponding range

$B(OH)_4^-$ and $B(OH)_3$. Between 0·1 and 2·1% B_2O_3 the data fit best the assumptions that boric acid and a univalent three-boron ion predominate in acidic solutions, that univalent and divalent three-boron ions and a divalent four-boron ion predominate when the Na_2O/B_2O_3 molar ratio is in the neighbourhood of 0·4 (pH near 8·8)[353, 356] (Fig. 12) and that a divalent four-boron ion and the monoborate ion predominate in the more alkaline solutions.[354] At concentrations 1·4–2·1% total B_2O_3, in the regions where the average charge per boron atom is near 0·1, the data are interpreted best by assuming a five-boron ion.[355] A five-boron ion was reported to be predominant in concentrated solutions at pH 6–8.[915] Using sodium or lithium bromide rather than sodium chlorate gave only small changes in the formation constants; using potassium bromide gave measurable differences.[354A] Recent acidity measurements at temperatures from 50° to 290°C have indicated a high probability that the monovalent two-boron and three-boron ions and either the divalent four-boron or trivalent five-boron ions exist[565A] (Fig. 13). The thermodynamic quantities ΔH°, ΔS° and ΔC_p° were derived for the equilibrium $B(OH)_3 + OH^- = B(OH)_4^-$ at infinite dilution.[565A]

In other work, formation constants of various polyborate ions were calculated at various temperatures from pH values in the titration of boric acid with metaborate, in the presence of sodium chloride, potassium chloride, sodium sulphate, cæsium iodide or sodium bromide. At 0·4M boron concentration the major polyborate ions were indicated to be $[B_3O_3(OH)_4]^-$ and $[B_4O_5(OH)_4]^{2-}$, with smaller amounts of $[B_3O_3(OH)_5]^{2-}$ and $[B_5O_6(OH)_4]^{2-}$.[792A]

The structures of the polyborate ions in solution have been regarded as probably similar to those of the polyborate ions found in and postulated for the crystalline hydrated borates. A divalent three-boron ion with six-membered ring structure (Fig. 14) has been found in the mineral meyerhofferite $2CaO,3B_2O_3,7H_2O$ and higher hydrates. A univalent three-boron ion with a similar ring structure (Fig. 15) has been postulated for gowerite, $CaO,3B_2O_3,5H_2O$.[160] The four-boron ion in solution may have the two-ring structure of the $[B_4O_5(OH)_4]^{2-}$ ion found in borax[584] (Fig. 5). The five-boron ion may have the two-ring structure (Fig. 8) of the ion found in potassium pentaborate tetrahydrate[933], although nuclear magnetic resonance studies make this appear doubtful.[603A] A summary of Ingri's work[353] includes a tabulation of equilibrium constants for the formation of the polyions

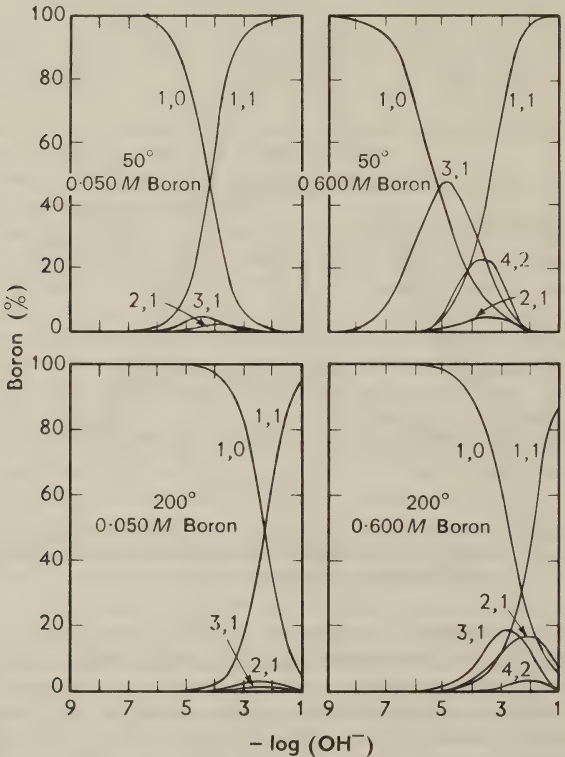

Fig. 13.—Distribution of boron among various ions in solutions containing 0·05M and 0·60M boron at 50° and 200°C.[565A] The species are represented by the notation (*x*, *y*) for the formula $B_x(OH)^{y-}_{3x+y}$

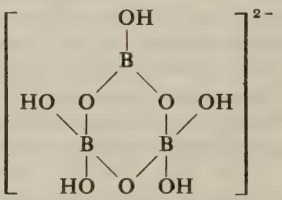

Fig. 14.—Divalent triborate ion, $B_3O_3(OH)_5^{2-}$, in meyerhofferite[160]

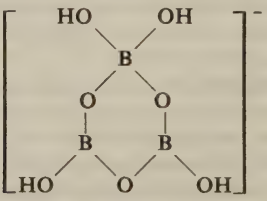

Fig. 15.—Univalent triborate ion, $B_3O_3(OH)_4^-$, postulated for gowerite[160]

and a diagram, for solutions containing 13·93 g of boric oxide per litre, showing the distribution of the boron among the various ions as a function of $-\log [OH^-]$ (Fig. 12).

A theoretical study, based on the hypothesis that $H_2B_4O_7$ is formed, gave results in agreement with the pH values and freezing points of partly neutralized boric acid solutions.[385]

SPECTRA AND N.M.R. STUDIES

Infra-red studies over a wide pH range indicated that at 0·25M-H_3BO_3 the maximum polyborate concentration, containing about 15% of the boron present, occurs at a pH of about 9.[288] These studies also confirmed that dissociation of the polyborate ions increased with increase in temperature or dilution.[288] In other work, infra-red spectra were interpreted to indicate a decrease in tetrahedrally coordinated boron with a decrease in pH, accompanied by formation of the ions $[B_3O_3(OH)_5]^{2-}$, $[B_4O_5(OH)_4]^{2-}$ and $[B_5O_6(OH)_4]^-$.[863] A decrease in the four-coordinated boron with time was observed.[863] The Raman spectra of sodium metaborate and borax solutions have been studied.[617A]

Nuclear magnetic resonance studies of ^{11}B in solutions of boric acid, metaborates, pentaborates and tetraborates agree with complete dissociation to H_3BO_3 and $B(OH)_4^-$ at low concentrations and formation of several polyborates in pentaborate and tetraborate solutions, at high concentrations.[579, 603A, 781A] The amounts of $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B_5O_6(OH)_4^-$ present in sodium pentaborate solutions up to 0·4M were calculated.[579] ^{11}B chemical shifts were determined for sodium metaborate, sodium and potassium pentaborate, and disodium and dipotassium tetraborate solutions.[627] Other n.m.r. studies agree with the presence of tetrahedral $B(OH)_4^-$ ions at high pH values and $B(OH)_3$ at low pH.[341]

CONDUCTIVITY

The electrical conductivity of sodium metaborate solutions (1–20% $NaBO_2$) has been determined at 20–300°C. At temperatures below 80°C, there is a maximum in the conductivity–concentration curve. At 25°C the maximum conductivity is at 15% $NaBO_2$; at 40°C it is at 17%.[522]

Menzel reviewed the published information up to 1927 on the conductivity of borate solutions and determined the conductivity of 0·02 to 0·8N-KBO_2, -$K_2B_4O_7$ and -KB_5O_8 solutions at 0°C.[562]

An experimental study of the conductivity of KBO_2, $LiBO_2$, $K_2O,2B_2O_3$, $Na_2O,2B_2O_3$, $Li_2O,2B_2O_3$, $Li_2O,5B_2O_3$, $Li_2O,8B_2O_3$, $Li_2O,167B_2O_3$, $Li_2O,16{\cdot}7B_2O_3$ and $Li_2O,600B_2O_3$ solutions at temperatures of 30–300°C has been made.[1167]

Other conductivity studies have been made[89, 260, 1115A], including an investigation of dipotassium tetraborate at 2–5000 p.p.m.[1134A] In thin films, the conductivity of sodium metaborate solutions is low.[1023] Other studies[389, 808, 813] indicated the presence of the monoborate ion in dilute alkali–metal borate solutions and the pentaborate ion in the presence of excess boric acid. From conductivity studies and boron volatility studies at high temperatures, the distribution of boron among the various ionic species was deduced.[1167]

Electrophoresis of a borate buffer (pH 8·6) on a paper strip has been found to cause a large change in the pH.[817] The relative difference in mobilities for the $^{10}BO_2^-$ and $^{11}BO_2^-$ ions was measured by electrophoresis.[645A] Other conductivity and electrodialysis studies have been made on solutions of sodium and potassium metaborate and of borax.[181] The equivalent conductivity of $B(OH)_4^-$ at 20°C is 61·6.[260] Electro-osmosis in 0·33M solutions of borax has been studied.[925] Electrodialysis studies using an ion-exchange membrane have shown that in borate solutions at pH 7·22 the polyborate ion is mainly the tetraborate ion.

The mobility of the anion in aqueous solutions of various metaborates, tetraborates and pentaborates was found to be 39–40 mho cm².[389] The mobilities of the anions of $K_2O,CaO,4B_2O_3,12H_2O$, $K_2O,SrO,4B_2O_3,14H_2O$ and $K_2O,BaO,4B_2O_3,14H_2O$ are 38·7 mho cm².[389A]

OTHER PHYSICAL PROPERTIES

Supersaturation

Borate solutions, especially those having a high solubility, supersaturate easily. They can be spray-dried to form amorphous products which will dissolve quickly without the temperature decrease which occurs when crystalline borate hydrates dissolve.[1063] These amorphous products can also contain sodium chlorate.[979] Supersaturated borate solutions can be formed by dissolving mixtures of boric acid and calcined borax without heating or cooling.[977]

A solution containing 40–80% of $NaBO_2$ at 100–180°C can be drum-dried at 130–200°C to form flakes having 0·1 to 0·7 molecules of water per molecule of $NaBO_2$.[1035]

Crystallization of supersaturated borax solutions has been inhibited by the presence of Fe^{3+}, Al^{3+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ca^{2+}, Mg^{2+} ions and anionic surface active agents.[978, 1059] In brines containing sodium and potassium chlorides, carbonates or sulphates, borax crystallization has been inhibited during the crystallization of other salts, by rosin, extract of creosote bush or other resinous material.[1004]

Solutions containing sodium borate–phosphate mixtures, in a ratio of about one phosphorus atom to four boron atoms, do not crystallize but tend to form films.[1015]

Sodium metaborate crystallization is inhibited by adding about 10% (dry weight) of sodium arsenite, sodium silicate, trisodium phosphate, potassium carbonate, potassium permanganate or ammonium iodide.[1023] Supersaturated borax solutions are stabilized by dichromate[1051] or sodium metasilicate.[1045, 1050, 1070] A mixture of equal weights of borax and sodium metasilicate ($Na_2SiO_3,5H_2O$) melted in the water of crystallization at about 100°C on stirring, formed a clear solution which was stable for more than 90 days. The solution dried to form a clear intumescent film.[1045] By rapid cooling, potassium chloride may be crystallized from solutions containing potassium chloride and borax which are supersaturated with borax.[956]

Viscosity and Density

Borax (0·5%) increased the kinematic viscosity of water by about 0·5%. Determinations have been made at concentrations below 1·5% at 60°, 80° and 100°F.[92] Other determinations[1117A] gave the values shown in Table XXIII. The kinematic viscosity of a borax–boric acid solution containing 0·474% of sodium oxide and 4·83% of boric oxide was determined to be: 0·7872 at 37·8°; 0·6444 at 48·89°; 0·5409 at 60·0°; 0·4619 at 71·1°; 0·4043 at 82·2°; and 0·3582 at 93·3°C.[1117A] Viscosity, density, electrical conductivity, f.p., b.p., coefficients of expansion and conductivity were measured on solutions of borax in water–ethanol–dioxan mixtures. One such solution had a f.p. of −46°C.[838] Curves showing the density of borax solutions at various temperatures have been published.[1201]

Table XXIII.—Kinematic Viscosity of Borax Solutions

Temperature, °C	Kinematic viscosity, centistokes			
Borax concentration	0%	1%	5%	10%
25	0·91	0·92	—	—
35	0·74	0·746	0·806	—
50	0·5672	0·5744	0·6146	0·6734
64	0·4564	0·4674	0·5044	0·5444
79	0·3742	0·3874	0·4160	0·4602

Surface Tension

Borax decreases the surface tension of water from 72·8 dynes cm^{-1} with no borax to 72·3 with 0·5% and 70·9 with 1·5% borax.[92] The surface tension of saturated borax solutions at 22°C is between 72 and 76 dynes cm^{-1}, and borax is therefore a non-creeping crystallizing salt. Solutions having surface tensions above 75–76 dynes cm^{-1} at 22°C tend to creep during crystallization.[425] The interfacial tension between borax solution (0·001–0·1M) and two asphalts at 85°C has been determined.[846]

Vapour Pressure and Volatility

Osmotic and activity coefficients for disodium and dipotassium tetraborates and sodium metaborate at 25°C have been derived from isopiestic measurements with sodium chloride as the reference salt.[650] Freezing-point determinations led to a revision of these activity coefficients for the tetraborates.[650A]

The critical temperature of 0·20M-$Na_2B_4O_7$ solution has been reported to be 29·8°C above that of pure water.[394]

The vapour pressure of a saturated borax solution was determined to be: 129·4 mm at 57·94°; 130 at 57·99°; 131·4 at 58·23°; 133·1 at 58·56°; 134·7 at 58·82°; 135·4 at 58·91°; and 138·2 at 59·42°C.[561]

A pressure–temperature curve was determined for saturated solutions of disodium octaborate, $Na_2O,4B_2O_3$, at temperatures from 374° to 600°C; apparently this anhydrous compound exists in equilibrium with its solution under these conditions. The pressure ranged from 47 to 150 bars at these temperatures.[580]

The volatility of borate from solutions has been used to determine the distribution of boron among the various ionic species.[1167] The effect of pH of the water on the concentration of boric acid in steam from boiling water at pressures 1–20 atm has been determined.[848, 851] In the pressure ranges 0·2 to 20 MN m^{-2} (2–200 bars), the coefficients (concentration in steam/concentration in water) for ammonium pentaborate, borax, sodium pentaborate and boric acid were nearly equal to (density of steam/density of water)$^{0 \cdot 9}$, as indicated by laboratory experiments.[849–51] At a pressure of 10 MN m^{-2} (100 bars) the apparent distribution coefficient for boric acid decreases from 0·10–0·11 at pH 8·6 to 0·02–0·03 at pH 11·2, and at pressures less than 0·2 MN m^{-2} (2 bars) there was some irregularity in the results.

A solution of borax, sprayed on an agitated bed of particles of anhydrous borax maintained at 400°–700°C was reported to produce an anhydrous product having a relatively high bulk-density, but the product was more hygroscopic than anhydrous borax produced by melting.[971]

Diffusion

Diffusion coefficients of borax and sodium pentaborate have been measured at 25–37°C in solutions containing 0–0·077 mole $litre^{-1}$.[681]

Index of Refraction

Refractometry calibration curves for borax have been published.[272] Data on aqueous borax solutions at 100°C are: 40% borax, 1·3598; 43%, 1·3644; 46%, 1·369.[1117A]

Chemical Reactions of Borates in Solution

In this section the reactions of the alkali metal borates in solution are discussed under the following headings: cation complexes; polyol complexes; reactions with acids; reactions with salts of alkali metals; reaction with salts of Group II metals and other metals; reactions with sulphur, oxides of carbon and peroxides; electrode reactions and electrolysis; corrosion inhibition; hydrothermal reactions; effect of borates on crystallization of other salts; removal of borates from solution; removal of impurities from borate solutions; and phase equilibrium in aqueous borate solutions.

CATION COMPLEXES

Borate ions in solution form complexes with many metal ions, with polyhydric compounds and with fluorides.[1130] The synthesis of the cationic complexes and their properties have been reviewed through 1969.[765A] Nuclear magnetic resonance studies of ^{11}B in boric acid confirm that the borate ion rather than boric acid forms the calcium complexes, as boric acid shows no chemical shift when calcium chloride is added (ref. 1078, p. 94). When calcium chloride is added to a borax solution there is at first an amorphous precipitate. This dissolves when a large excess of calcium is added, because a calcium–borate complex is formed. The apparent pK of boric acid is thereby decreased from 9·2 in water to about 4 in a solution 5·4M in calcium chloride, so that boric acid may be titrated to a pH 7 end-point.[733]

A variety of salts affect the phenolphthalein end-point in the titration of boric acid with sodium hydroxide in the presence of ethylene glycol.[765] Salts having a large effect are lithium chloride, calcium chloride, barium chloride, sodium bromide, sodium iodide, calcium nitrate and barium nitrate. Salts having a moderate effect are sodium chloride, sodium nitrate, potassium bromide and potassium iodide; little effect was shown by potassium nitrate, sodium sulphate and potassium sulphate. There was a relationship between the acidifying effect and the hydration energy of the ions.[765] A theory was proposed that the acidifying effect was due to the different properties of water of hydration of the positive and negative ions[765], but complex formation may have been involved in some cases.

A study has indicated the existence of $FeBO_2^{2+}$ and $Fe(BO_2)^+$ [756A] and a procedure has been developed for the determination of iron by potentiometric titration with borax solution.[758] Potentiometric titrations of aluminium nitrate and $Al(OAc)_2^+$ with borax solutions have been interpreted as indicating the existence of the complexes $AlBO_2^{2+}$, $Al(BO_2)_2^+$, $Al(BO_2)_3$ and $Al(BO_2)_6^{3-}$. Instability constants of aluminium borate complexes have been determined from potentiometric titrations and from spectrophotometric data in systems containing Fe^{3+}.[757] This work, however, has been questioned.[37A, 1102]

The solubility of divalent cobalt in borax solutions increases on addition of boric acid. Polarographic investigations have shown that the aquo-cobalt complex is reduced at the mercury surface, but not the cobaltous–borate complex.[647] The complexes $Pb(BO_2)_3^-$ and $PbBO_2^+$ exist.[756] The existence of $Co(BO_2)_4^{2-}$ and $Ni(BO_2)_3^-$ has been proved by ion-transfer experiments, and their instability constants were evaluated from solubility and spectrophotometric experiments.[759]

Conductivity and freezing-point studies have indicated that magnesium–borate complexes are formed.[168A]

Zinc and cadmium form borate complex ions.[1101, 929]

Silver- and glass-electrode measurements have indicated that $AgBO_2$, a weak uncharged complex, is formed in solution.[322A]

POLYOL COMPLEXES

Complexes are also formed with certain polyhydroxy organic compounds. Reviews on the chemistry and structure of these complexes were published in 1964[1116] and 1967.[902] Although boric acid alone is too weak to be determined by titration with a strong base, the acidity is greatly increased by the addition of mannitol, glycerol, sorbitol or other similar compounds. Titration curves (of which those in Fig. 16 are typical) of boric acid in the presence of a variety of glycols and sugars[63A, 550] show that only a few of the compounds investigated would increase the acidity sufficiently for an accurate titration of boric acid to the phenolphthalein end-point. Mannitol gives the sharpest end-point.[550] For titration of the borate with hydroxide to phenolphthalein, two moles of glycerol are needed per mole of boric acid, and eight moles of glycerol per mole of borax. An excess of glycerol is preferable.[59]

With four moles of glycerol a strongly acidic glyceroboric acid is formed. Glycerol solutions containing 2 to 20% of borax became more acidic with increasing glycerol content.[233, 866] With 20% or 86% of glycerol an increase of borax content gives practically no change in pH.[233] Some pH values in solutions of borax containing glycerol[866] are shown in Table XXIV.

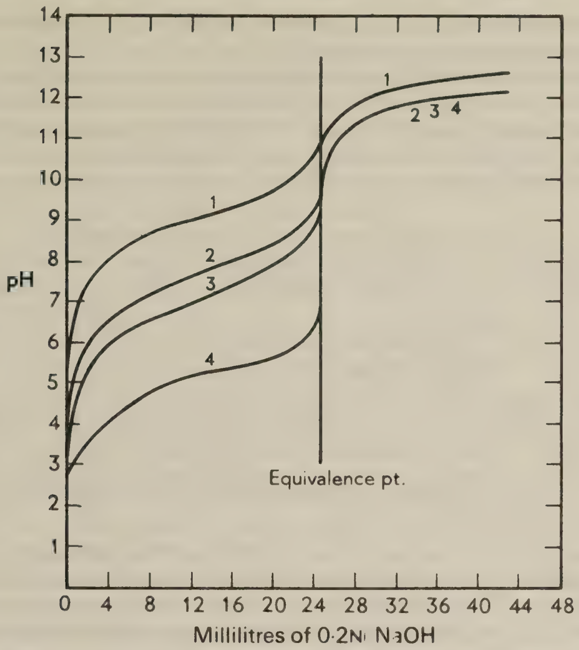

FIG. 16.—Titration of boric acid in the presence of polyalcohols. (1) Acid alone. (2) Erythritol added. (3) Mannitol added

Table XXIV.—pH Values of Borax–Water–Glycerol Solutions at ~15°C[866]

% Glycerol	2% Borax	6% Borax	10% Borax
5	7·90	8·3	8·7
10	7·25	7·60	8·0
20	6·55	6·75	7·05
30	6·10	6·25	6·45
40	5·75	5·9	6·05
60	5·25	5·4	5·45
85·8	4·8	4·9	5·0

Carbon dioxide is evolved when glycerol and borax are mixed with water and sodium bicarbonate.[59]

Complex formation in solutions containing sodium metaborate and various polyols has been studied by means of Raman spectra.[622A] Evidence was found for the existence of both the 1:1 and 2:1 (diol:boron) complexes in concentrated aqueous solutions containing 1,2-ethanediol and sodium metaborate.[622A]

Freezing-point and electrical conductivity studies have been made of the complexes of borax and various polyhydroxy-alcohols.[376] The change in pH of borax solutions with temperature has been determined in the presence of many polyhydric alcohols and organic acids.[549] The formation constants of many borate complexes have been determined from pH measurements.[30, 714]

Proton magnetic resonance studies showed that no complex formation occurred between mannitol and boric acid in deuterium oxide, if enough deuterium chloride was present to repress the boric acid ionization.[416A] Cryoscopic studies in calcium chloride hexahydrate showed that no complex was formed in the boric acid–mannitol–$CaCl_2,6H_2O$ system, but that complexing did occur in the lithium metaborate–mannitol–$CaCl_2,6H_2O$ system.[520] An investigation of the mannitol–borax and sorbitol–borax complexes by the dilatometric method agreed with the formation of both mono- and bi-chelated compounds.[793]

Conductimetric and pH studies confirmed that the mono- and bi-chelate complexes are formed with mannitol and that the mannitol–borate complex is present in appreciable amounts only in basic solutions.[210, 416, 708A] There is now wide agreement that the borate ion, rather than boric acid, forms the complexes.[210, 714, 858] The complexes would thus be formed as in Fig. 17. Nuclear magnetic resonance studies[627] have shown that the ^{11}B resonance line of boric acid solution did not shift when mannitol was added. This method is quite sensitive to a change of boron from three to four coordination. The mannitol–borax reaction has also been studied by chromatography.[922A] The heat of reaction of mannitol with sodium metaborate has been measured.[616]

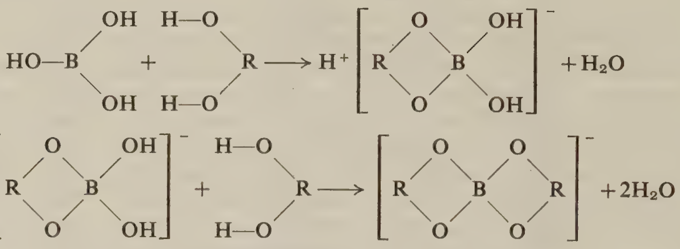

FIG. 17.—Formation of mono- and bi-chelate complexes

The formation constants K_1 and K_2 of the 1:1 and 2:1 mannitol–borate complexes have been investigated by pH measurements in several laboratories[210, 1221, 616, 616A, 708A, 845A] with often divergent results, sometimes apparently due to misinterpretation of the experimental data.[139, 416A, 670] A recent investigation[416A] gave 2·79 to 4·98 as reliable values for log K_1 and log K_2, respectively, in agreement with the values 2·75 and 5·06 given in a previous paper[845A], and showed that experimental data in the other papers, when recalculated, gave consistent values for K_2. A review of the literature on the boric acid–borate–mannitol system discussed a difficulty in interpreting its behaviour.[670]

Freezing-point measurements have shown compound formation in borax–sugar solutions.[501] Glucose and maltose migrate towards the anode in the presence of borax.[179] The extent of chelate formation with hexoses varies greatly with the configuration of the hydroxyl groups[30], as indicated by potentiometric titrations. This relationship has been studied by many investigators, especially by Böeseken and co-workers, utilizing conductivity measurements.[99, 99A] The effect of sodium and potassium borate on the optical rotation of carbohydrates has been studied.[179, 344, 361, 502] The rotation of glucose–borax solutions can vary from $+52°$ to $-8°$ depending on the concentrations.[179] Adding borax to glucose causes a large change in the rotation.[596] When sodium metaborate is added to glucose or xylose, two moles of sodium metaborate per mole of glucose and one mole of sodium metaborate per mole of xylose give the maximum change.[593] Borate combines with the *cis*-vicinal hydroxyl groups of sugars; mutarotation can be observed after acidification.[393A] N.m.r. studies of borate complex formation can be used to detect neighbouring *cis*-diol groups in carbohydrates.[880A]

Borax has a marked effect on the rotatory dispersion curves of glucose, galactose, mannose, fructose, arabinose, xylose and sorbose, owing to complex formation. There was no effect in the case of the disaccharides lactose, maltose and sucrose or purine nucleosides, but there was a marked decrease in the rotation of pyrimidine nucleosides.[661] Borate combines with cellulose.[707]

Various sugars have been added to sodium hydroxide solutions containing 1% of boric acid, and the decrease in pH noted. No decrease was observed when the pH of the original solution was as low as 3.[836] In fructose–Li_2O–B_2O_3 solutions, polarographic studies indicated that a 1:1 fructose–borate complex is predominant.[816] The dissociation constants of the 1:1 and 2:1 fructose–borate complexes have been evaluated by pH studies.[845A] Polarographic studies indicated that the borate is bonded to the fructose through the 2-keto-position.[845A]

The effect of borate on the oxidation of sugars has been studied.[472A] The rate of oxidation is usually decreased by alkaline borates, and the relative quantities of oxidation products are probably changed.[499] Oxidation of glucose by alkaline copper solutions does not occur if enough borate is present.[514]

Tests of borax–dextrin–sodium hydroxide water adhesives have been interpreted to indicate probable formation of a chain of alternate dextrin and metaborate ions.[622] The maximum viscosity was reached with 2·4 to 2·85 moles of sodium hydroxide per mole of borax.

The levulose content of invert sugar has been determined by titration with sodium hydroxide in the presence of boric acid and phenolphthalein.[277]

Solutions of sugar or other polyol-borate complexes were passed through strong-base ion exchange columns, and the absorbed complex ions were then eluted by a borate solution, resulting in a separation of the various sugars.[401] Similar studies of carbohydrate separation have been made using a charcoal column and paper chromatography[52], paper ionophoresis[259] and gas–liquid chromatography.[361A] Sugars which have been separated as their borate complexes by ion exchange can be determined by refractometry.[511A]

Ionophoresis in a borate buffer at pH 10 has been proposed for determining the structure of polysaccharides.[259]

More carbohydrate was extracted from a wood cellulose by 16% potassium hydroxide containing 3–4% of boric acid, than by 16% potassium hydroxide alone.[369] Borax accelerates the reaction of cyanides with reducing sugars.[109] Enzymatic isomerization of glucose to produce fructose takes place in the presence of borate.[1137, 949A]

Polarimetric studies on solutions of boric acid, borax or potassium metaborate with mannitol, glucose, tartaric acid, sodium tartrate or calcium gluconate have indicated that complex formation may occur between boric acid and the carboxylate ion as well as between the $B(OH)_4^-$ ion and hydroxyl groups.[858] Sodium metaborate in aqueous solution with sodium gluconate forms a 1:1 ($BO_2^- : C_6H_{11}O_7^-$) complex and under some conditions a 1:2 complex, as indicated by conductivity and refractive-index studies.[814A] The 1:1 complex was isolated as a white glassy substance.[1173] Further studies were made of sodium borogluconate.[831A] Double salts with alkaline-earth metals were also prepared.[1173] In solutions of metaborates and ascorbates, there is evidence for the formation of complex ions with metaborate:-ascorbate molar ratios of 1:2[1104, 813A] and 1:1 and 1:2[813A, 1106]; the acids form complexes with similar ratios.[1105] Solid alkali bis-(ascorbato)-borates are precipitated from alcoholic ascorbic acid–boric acid solutions with sodium or potassium hydroxides.[431A] Crystalline dipinacol borates, $MBO_2,2C_6H_{12}O,4H_2O$, where M is Li, Na or K, have been prepared by adding an alkali hydroxide to a boric acid–pinacol hydrate solution.[378A] The relation of borate ions to gels of a galactomannan solution has been discussed.[163A]

The formation of borate complexes with erythromycin[337], with 2,3-dihydroxy-6-naphthalene sulphonic acid[604A] and with 2,3-naphthalene diol[31A] has been studied. The borax–chloramphenicol complex[116] and the effect of borate on the polysaccharide protein and antigen–antibody reactions[815A] have been studied. Borate inhibits precipitation between anticarbohydrate antibodies and various polysaccharides.[815A]

Polyvinyl alcohol gives a gelatinous substance with borax.[18, 624] The viscosity of these systems in water has been investigated.[347A] When polyvinyl alcohol film was immersed in borax solution, swelling increased with an increase in borax concentration, and the film dissolved in 10% borax solution. An *X*-ray fibre diagram of the complex compound was obtained.[624–5] Polyvinyl alcohol (1·5–2·0% concentration) with sodium metaborate and sodium hydroxide gave an elastic gel.[834] Structural changes in sodium metaborate–polyvinyl alcohol solutions have been studied in relation to rheological behaviour.[110] The viscosity and pH of aqueous polyvinyl alcohol–sodium borate mixtures were measured at various concentrations and pH values.[917] The gelation of a dispersion of guanosine in a borate solution has been studied.[625A] Inhibiting and softening properties of polyoxy-complexes have been studied.[374A]

Borax does not react with a 3% polyacrolein solution.[18]

The amount of dialdehyde starch dissolving in 15–120 min in 0·5, 1·0, and 5·0% borax solution at 55°C has been determined.[34]

Rutin and quercetin have bonds with the metaborate ion in two places, as is shown by methylation and hydrolysis experiments.[764]

Potassium tetraborate reacts with *N*-acetylhexosamines to form chromogens.[626] Borax and potassium borates, with polyhydroxy-compounds, have been patented as constituents of non-crystallizing developers for diazotype materials, which do not cause discoloration.[985]

Addition of borate made few changes in the ultra-violet spectrum of catechol.[311] Borax increases the sorption of catechol on a weak-base ion-exchange resin.[311] Separations of other polyol isomers have been made by selective sodium borate complex formations with the *cis*-isomers.[191–2] Several cyclic polyol complexes were crystallized and their structures proved from thermal dehydration curves.[192] The boropentaerythritols $Li_2O,B_2O_3,2C_5H_8O_2,9H_2O$ and $Na_2O,B_2O_3,2C_5H_8O_3,9H_2O$ have been crystallized.[1199A] The borate ion forms chelates with one and two molecules of pentaerythritol, and the chelation constants have been determined.[31] Xylitol forms complexes with the alkali borates, and their infra-red spectra have been studied.[664A, 1088–9]

Borates can be extracted from alkaline[154, 416, 968, 970] or acidic[1202] brines with a solution of certain polyols in kerosene (see p. 432). Experiments on the extraction of borate using 2,2-diethyl propanediol-1,3 and 2-ethylhexanediol-1,3 in chloroform at pH 2 to 12 indicated that no complexes were formed with borate ion in the aqueous layer. A 1:2 boric acid–diol complex was, however, formed in the chloroform phase in two steps.[226]

Alkali-metal salts of the complexes of boric acid with hydroxyacids have been known for a long time, and their methods of preparation and properties have been reviewed.[1116] Borotartrates of sodium and lithium can be prepared by heating a boric acid–tartaric acid mixture with simultaneous neutralization with sodium or lithium carbonate.[807] Conductometric and polarimetric studies have indicated that borotartrate complexes with a tartrate–boron ratio of one are formed in sodium monoborate or borax solutions. Complexes having a higher boron content are also formed in these solutions, and in sodium pentaborate solutions.[814] A variety of sodium borotartrates have been prepared by evaporating solutions containing sodium borates and tartaric acid.[372]

In a study of solubilities in the system Na_2O–B_2O_3–trihydroxy glutaric acid–water, the compounds $2Na_2O,B_2O_3,2C_5H_6O_6,3H_2O$ and $Na_2O,B_2O_3,C_5H_6O_6,3H_2O$ crystallized. The solubility was increased by the formation of the complexes.[666] The DTA and DTG curves and the infra-red spectra of these compounds were studied, and structures were proposed.[667]

Borax reacts with aqueous ammonium sulphate or chloride and ethylene glycol to form glycol borate, from which methyl borate can be formed by transesterification.[1150]

A borate buffer of pH 7·62 in the presence of oxygen gives irreversible photobleaching of methylene blue.[861]

The lowest borax concentration which will precipitate solutions of ethyl hydroxyethyl cellulose was determined.[371] The coagulation effect of borax on zinc hydroxide and ferric hydroxide sols suggested that the anions in a borax solution are bivalent.[89]

From experiments on the sorption of borate ions on an ion-exchange resin in the chloride form, it was calculated that a mixture of $B_5O_8^-$, $B_4O_7^{2-}$ (or $HB_5O_9^{2-}$) and monoborate ions was sorbed.[237]

REACTIONS WITH ACIDS AND AMMONIUM SULPHATE

Borax reacts with sulphuric acid to precipitate boric acid. A cyclic process has been patented in which borax and water are added to the solution after removal of the precipitated boric acid. By this means the liquor can be further cooled to crystallize Glauber's salt without further crystallization of boric acid.[953] Borax and sulphuric acid, when added to a saturated sodium sulphate solution at 100°C, precipitate anhydrous sodium sulphate. When the solution is cooled to 30°–35°C, boric acid free from sulphate is formed.[984]

Borax reacts with nitric acid to give boric acid and sodium nitrate. If the reaction is carried out in a liquor saturated with both sodium and potassium nitrates, the boric acid crystals float and the sodium nitrate sinks, and thus the products can be separated without fractional crystallization.[1061]

Borax in solution reacts with carbon dioxide and methanol to form trimethyl borate, which may be distilled out as the methanol azeotrope.[1148, 1152]

Borax in solution reacts with sulphur dioxide to form boric acid crystals and sodium sulphite in solution. After separation of the boric acid the mother liquor may be treated with more sulphur dioxide to give sodium bisulphite.[980]

Borax reacts with ammonium sulphate in a hot solution to give ammonia, sodium sulphate and boric acid, and a process has been worked out[1008] for producing these materials.

According to a phase diagram of the HBO_2–NaF–H_2O system at 30°C[606], borax reacts with hydrofluoric acid to give sodium fluoborate and boric acid, rather than $Na_2O(BF_3)_4$ as previously reported.[1007] The BF_3OH^- ion is formed under some conditions.[316] Addition of hydrofluoric and sulphuric acids to borax gives boron trifluoride.[1007] With an excess of hydrofluoric acid, the sodium content of sodium borates can be quantitatively determined as sodium fluoborate, by evaporation on a steam bath and drying to constant weight at 110°C.[581] Borax has been proposed as a reagent to react with hydrofluoric acid in the recovery of uranium.[1130]

Powdered arsenious acid largely dissolved when digested with a saturated borax solution. When this solution was evaporated, a brittle transparent pale-yellow mass of gummy appearance was formed, which dissolved in a small amount of water to form a syrup. This syrup solidified when chilled to give a crystalline mass, containing about five equivalents of arsenous oxide, six of boric oxide, three of sodium oxide and ten of water.[741]

Tannic and gallic acids react with borax like arsenious acid, gallic acid forming a gummy mass and tannic acid a yellow powder.[741] Margaric, stearic and oleic acids dissolve in considerable amounts.[741]

Potassium pentaborate will react with phosphoric acid to give dipotassium phosphate and with nitric acid to give potassium nitrate.[306]

Lithium borate solutions (2·5%) dissolve 0·52% of uric acid at pH 7 and about 1·5% at pH 9, but higher lithium borate concentrations do not increase the solubility further.[621]

REACTIONS WITH ALKALI-METAL COMPOUNDS

Potassium metaborate solutions react with lithium hydroxide to give well-formed crystals of lithium metaborate, $LiB(OH)_4$. Rubidium and cæsium metaborates can be prepared by the same method.[634]

Borax in solution reacts with potassium chloride to crystallize dipotassium tetraborate, $K_2O,2B_2O_3,4H_2O$. In the presence of ammonia the yield is increased, and a process utilizing it has been patented.[965] The mother liquor from the borax–potassium chloride reaction may be carbonated to form sodium bicarbonate and KB_5O_8,$4H_2O$.[963]

Borax does not react with sodium carbonate in solution at atmospheric pressure, but if the solution is heated to a temperature above 120°C, preferably 150–200°C, and the carbon dioxide is allowed to escape at 40–210 lb in^{-2}, sodium metaborate is obtained in solution.[951]

Borax, potassium chloride and sulphuric acid, dissolved in water and heated, react to form potassium pentaborate, $KB_5O_8,4H_2O$.[1028]

Sodium metaborate reacts with trisodium phosphate in solution to form a double salt, $NaBO_2,Na_3PO_4,18H_2O$ which has a solubility of 12·8 parts per 100 parts of water at 25°C and 20·8 parts per 100 parts of water at 35°C.[955] In solutions saturated with other sodium salts, the solubility is less. The amount of the 18-hydrate dissolving in saturated salt solutions, in parts per 100 parts of water, is: sodium chloride at 25°C, 7·6; trisodium phosphate at 25°C, 1·9; at 35°C, 3·3; sodium metaborate at 25°C, 0·2; at 35°C, 1·0.[955]

Borates increase the rate of formation of iodate from iodide and iodine. In a series of experiments in which the sum of the molar concentrations of potassium hydroxide and boric acid was constant, the maximum rate of iodate formation occurred at a molar ratio ($K_2O:B_2O_3$) of 1·4.[511]

REACTIONS WITH SALTS OF GROUP II METALS

Warm borax solutions react with solutions of soluble salts of calcium, magnesium, barium, zinc and cadmium to give gel-like precipitates which can be dewatered and pressed into shapes for a radiation shield.[92A]

Borax and magnesium chloride solutions form an amorphous precipitate which crystallizes in the presence of excess magnesium chloride to form pinnoite, $MgB_2O_4,3H_2O$, within about a week after seeding.[1107A]

Borax and magnesium sulphate in solution at 35°C give orthorhombic crystals of inderite, $2MgO,3B_2O_3,15H_2O$.[247A] Potassium metaborate solution reacts with inderite to give magnesium hydroxide.[467]

Dipotassium tetraborate ($K_2B_4O_7$) solution reacts with magnesium sulphate solution to give $K_2O,MgO,3B_2O_3,15H_2O$ (specific gravity 1·91)[388, 1107A] in several days.

When borax is added to milk of lime, the pH is decreased.[845] A suspension of four molecules of borax and two molecules of hydrated lime in six litres of water forms colloidal ulexite at room temperature in several days; this product is useful in ceramics.[312A]

A solution of borax and sufficient sodium hydroxide to give a pH higher than 11 after reaction, reacts with alkaline–earth chlorides or hydroxides to give an amorphous precipitate, which crystallizes to form the alkaline earth metaborate, MB_2O_4,nH_2O.[1107A] With an excess of borax and boric acid, at a pH between 3·5 and 8, the amorphous precipitate first formed crystallizes to form the hexaborate, MB_6O_{10},nH_2O.[1107A] Double borates are obtained by using the proper excess of borax and boric acid.[1107A]

A solution of borax and sodium hydroxide (molar ratio $B_2O_3:Na_2O$ 0·93–0·5) with calcium chloride solution gives an amorphous precipitate which forms crystals of $CaB_2O_4,6H_2O$ up to 2 mm in size within a few hours.[1107A]

An aqueous mixture of borax, calcium hydroxide and calcium sulphate or chloride with[635, 1196] or without[1197] the addition of sodium hydroxide will react at temperatures below about 25°C to form crystalline $CaB_2O_4,6H_2O$. At higher temperatures, $CaB_2O_4,4H_2O$ is formed. Sodium metaborate solutions, with or without sodium hydroxide, do not react with calcium metaborate.[467] $CaHBO_3$ is formed when sodium metaborate solution is mixed with slaked lime and concentrated at 100°C.[486A] Sodium metaborate solution, added to calcium chloride solution at room temperature, gave a product having a composition similar to pandermite, $4CaO,5B_2O_3,7H_2O$.[181A] Sodium metaborate solutions react with calcium salts to form $CaB_2O_4,6H_2O$ at room temperature or below.[635] An excess of borax solution, preferably with sodium hydroxide to give 1·7 moles of boric oxide per mole of sodium oxide, reacts with calcium chloride solution to give crystals of ulexite, $NaCaB_5O_9,8H_2O$ within a day.[1107A]

In the $Na_2O–B_2O_3–H_2O$, $K_2O–B_2O_3–H_2O$ and $(NH_4)_2O–B_2O_3–H_2O$ systems (containing small amounts of lime) at 25°C, the regions where $CaB_2O_4,4H_2O$, $CaB_2O_4,6H_2O$, $Na_2O,2CaO,5B_2O_3,6H_2O$ (ulexite), $2CaO,3B_2O_3,13H_2O$ (inyoite),

$K_2O,CaO,4B_2O_3,12H_2O$, and $(NH_4)_2O,CaO,4B_2O_3,12H_2O$ are formed have been determined. This was done by adding a precipitate of amorphous calcium borate to these solutions and agitating for periods up to 15 days.[281A] Further studies have been made of the conditions for the formation of $CaB_2O_4,4H_2O$ and $CaB_2O_4,6H_2O$.[1242]

Solutions of potassium, rubidium or cæsium tetraborate, containing two moles of $K_2O,2B_2O_3$ [283], $Rb_2O,2B_2O_3$ [284] or $Cs_2O,2B_2O_3$ [284] react with one mole of alkaline-earth metal chloride to give precipitates which are usually amorphous at first, but which crystallize on standing to form $K_2O,CaO,4B_2O_3,12H_2O$ [283], $Rb_2O,CaO,4B_2O_3,12H_2O$ [284], $Cs_2O,CaO,4B_2O_3,12H_2O$ [284], $Rb_2O,SrO,4B_2O_3,12H_2O$ [284] or $Cs_2O,SrO,4B_2O_3,12H_2O$.[284] The solubility of $K_2O,CaO,4B_2O_3,12H_2O$ is 7·3 g per litre at 20°. Its density is 1·793. Its unit-cell dimensions and indexes of refraction have been determined.[283]

Borax and $CaB_2O_4,6H_2O$ in a sodium chloride solution at 20°C or 40°C slowly form ulexite, $Na_2O,2CaO,5B_2O_3,16H_2O$.[467, 561]

Borax reacted with $CaSO_4,2H_2O$ and deuterium oxide at 68° to give $2CaO,3B_2O_3,7D_2O$. This compound reacted with $Na_2B_4O_7,10D_2O$ in deuterium oxide at 68°C, when seeded with colemanite, to give deuterated colemanite.[1136]

Potassium pentaborate in solution or suspension reacts with hydrated lime to give potassium hydroxide solution containing some borate and a calcium borate precipitate.[1006, 1037] When the potassium pentaborate solution contained 14% of boric oxide and 0·86% of ammonia, less than 3% of its original boric oxide content was left in the solution. The lime was added in two portions of 0·745 and 0·39 moles, respectively, per mole of original boric oxide, and the mixture was heated 15 h at 100°C or 6 h at 150°C and filtered after each portion was added. After the first filtration, the precipitate was washed with a weight of water equal to the weight of the original solution, the wash water being added to the filtrate.[1037]

Borax solution added to strontium chloride solution gives a precipitate of strontium borate.[181A] Borax, sodium hydroxide and strontium chloride in solution form crystals of $Na_2O,2SrO,5B_2O_3,16H_2O$ analogous to ulexite, in a week.[805, 1107A] A solution of borax and sodium hydroxide at a pH of 11·4–12·0 reacts with a solution of strontium nitrate at 60°C to give crystals of strontium diborate, $SrO,B_2O_3,4H_2O$, within half an hour.[1107A] At lower pH values, a mixture of the diborate and an acid borate is obtained.[282]

Borax solution added to barium chloride solution precipitates a barium borate.[181A] A borax–sodium hydroxide solution treated with barium chloride solution gives a flaky amorphous precipitate which crystallizes after a few hours, if the pH is maintained above 11, to form barium metaborate, $BaB_2O_4,4H_2O$.[879A, 1107A] A sodium borate solution (3·7 moles of boric oxide per mole of sodium oxide) added to barium sulphide solution at 57°–70°C and heated 3 h at 125°–140°C, forms a compound of the approximate composition BaO,B_2O_3,H_2O.[1184–5] Borax solution added to concentrated barium sulphide solution gives a precipitate of barium metaborate.[1186] Dipotassium tetraborate solution reacts with barium chloride solution, with seeding, to give crystalline $K_2O,BaO,4B_2O_3,14H_2O$.[387]

Traces of borate can be precipitated in 15% ethanol solution as barium borotartrate and then determined by measuring the barium in the precipitate by *X*-ray fluorescence.[514A]

REACTIONS WITH SALTS OF OTHER METALS

Borax generally reacts with heavy-metal salt solutions to give amorphous heavy-metal borates; crystalline heavy-metal borates are obtained from boric acid solutions.[1107A]

Borax solution, when added to an aluminium chloride solution, forms a stable thixotropic gel.[597] With aluminium nitrate, borax is said to form $Al(BO_2)_3,Al(OH)_3,4H_2O$.[757] An 'aluminium borate' is said to be produced by precipitating a solution of 115 parts of borax with a solution of 67 parts of crystalline aluminium sulphate, and washing and drying the precipitate.[1084] Mixing 0·2N-$Al(NO_3)_3$ and 0·2N-

$Na_2B_4O_7$ or -$K_2B_4O_7$ in volume ratios 2:1 to 1:6 gives white amorphous precipitates of composition $Al_2O_3,B_2O_3,2H_2O$ to $6H_2O$.[1222] Alkali borates, digested with aluminium fluoride, give insoluble Na_3AlF_6 and boric acid in solution.[1002]

Disodium, dipotassium and diammonium tetraborate solutions react with cadmium chloride solutions to give amorphous precipitates of variable composition. After a time, these change into definite crystalline borates such as $2CdO,3B_2O_3,7H_2O$ and $K_2O,CdO,4B_2O_3,KCl,5H_2O$[668], or can be converted into $[Cd(NH_3)_3H_2O]B_4O_7,6H_2O$.[399] Dipotassium tetraborate, boric acid and cadmium sulphate react in solution to give $K_2O,CdO,6B_2O_3,10H_2O$, which forms rather rapidly at 50°C.[665]

With an excess of borax, solutions of cobalt, magnesium, manganese or nickel salts give amorphous precipitates of varying composition, which will dissolve in boric acid and form the crystalline hexaborates MB_6O_{10},nH_2O in a day or two.[1107A]

Cobaltous chloride solution added to borax solution gives amorphous $CoB_2O_4,3H_2O$ which changes to $CoB_2O_4,2H_2O$ on ageing.[1223] With an excess of borax the precipitate contains more boric oxide. If boric acid is present, $CoB_6O_{10},8H_2O$ is formed.[1107A] When cobaltous chloride solutions are added to potassium borate solutions having a pH above 8 with good agitation, amorphous $CoB_2O_4,3H_2O$ is formed which changes to $CoB_2O_4,2H_2O$. If the pH of the borate is 7 to 8, $K_2O,CoO,6B_2O_3,11H_2O$[386, 1107A] is formed, and if the pH is below 6, crystalline cobalt hexaborate, $CoB_6H_{10},8H_2O$ is formed.[386]

Cupric chloride solution with borax gives a copper borate which has the composition $3CuO,2B_2O_3,3H_2O$ at first, and changes to $2CuO,B_2O_3,H_2O$ over a period of time.[100A] A crystalline sodium copper borate having the composition $2Na_2O,4CuO,9B_2O_3,38H_2O$ has been prepared.[708] A study of the reaction of potassium tetraborate with copper salts has been made.[276]

Ferric borate sols, positive or negative, can be made by adding borax solution to ferric chloride solution and dialyzing or dispersing under various conditions.[599]

Sodium metaborate reacts with gadolinium[663A] and lanthanum[1087] in solution to form the metaborates; these metals have been determined by conductometric titration with sodium metaborate in 50% ethanol.[663A, 1087]

Solutions of $K_2O,2B_2O_3$ or $Na_2O,5B_2O_3$, added to lead chloride, bromide or iodide solutions gave precipitates of the composition PbX_2,PbO,B_2O_3,H_2O.[696]

Borax solutions react with solutions of manganous salts at room temperature to give amorphous but easily filterable borates of manganese, having a variable composition depending largely on the ratio of the reactants.[323] If the molar ratio B_2O_3:Mn of the reactants is 1:1, the precipitate has the molar ratio 1·24:1; if the molar ratio of the reactants is 2:1, that of the precipitate is 1·57:1 ($2MnO,3B_2O_3$,aq).[1107A] Further, if the molar proportions B_2O_3:Mn:KOH of 1:1:1 are taken, the precipitate has the molar ratio (B_2O_3:Mn) of 1·03:1.[1107A] $K_2B_4O_7$–boric acid solutions, with manganese or dimanganese hexaborate, give crystalline $K_2O,MnO,6B_2O_3,11H_2O$[1107A], but a better method of preparation uses boric acid, manganese chloride, and potassium hydroxide.[1107A] Borax has no effect on the atmospheric oxidation of manganous hydroxide.[211]

Mercuric chloride with borax forms a red precipitate of basic mercuric chloride.[744]

Dilute sodium borate solution gives an intense blue, 'boromolybdic blue', when a sulpho-molybdic reagent is added and reduced. A mixture of sodium borate, a mineral acid, alkali molybdate and ether, agitated in sunlight, gives the same product. When purified by extraction, the boromolybdic blue is not stable; sodium borate added to its aqueous solution, prevents its decomposition.[185]

Borax and nickel salts give products of variable composition, depending on conditions.[1107A] Borax, mixed with a 0·1N solution of nickel chloride gave a precipitate of $NiO,B_2O_3,3H_2O$, which changed to $NiO,B_2O_3,2H_2O$ after ageing.[1223] Nickel chloride solutions 0·1M or stronger gave $2NiO,3B_2O_3$,aq.[320] When borax was added to a solution of nickel sulphate in concentrated ammonia at 80°–90°C and the solution was cooled, $Ni(NH_3)_4B_4O_7,4H_2O$ crystals were formed.[459A] When borax was added to a warm nickel sulphate–boric acid solution, $NiB_6O_{10},10H_2O$ was formed.[436]

When a solution containing boric acid and silver nitrate is titrated with sodium hydroxide, the first precipitate is white silver monoborate, $AgBO_2$. When larger amounts of hydroxide, approximately equal to the borate present, are added, a brown silver oxide precipitate is formed.[833] When silver nitrate is added to borax–boric acid mixtures in which the $B_2O_3{:}Na_2O$ molar ratio is greater than five, the precipitate has the composition $Ag_2O,2B_2O_3,2H_2O$.[1093] Recent work indicated that a phase of composition $Ag_2B_4O_7,xH_2O$ was apparently stable, and that there was evidence for the neutral complex $AgBO_2$ in solution.[322A] A white precipitate, which occurred in the more acidic solutions, was amorphous to *X*-rays.[322A]

Sodium metaborate and thallous nitrate solutions, mixed in equimolar proportions, give Tl_2O,B_2O_3,H_2O.[248] Borax and thallous nitrate solutions give $Tl_2O,2B_2O_3,2H_2O$.[248]

When a borax solution is added to a thorium nitrate solution, an amorphous gel is formed, which when fired forms thorium borate and thoria.[1197A] If the gel is dialyzed, a clear, colourless sol is produced.[598]

A mixture of hot 0·1M borax solution and hot 0·15M zinc nitrate solution was said to form crystalline ZnO,B_2O_3,H_2O after standing for one day[1101], but the existence of this compound could not be confirmed by other authors who obtained only amorphous products when borax and zinc sulphate ($B/Zn = 2$, 4 and 6) were used.[481A] Borax reacts with zinc sulphate solution and zinc oxide (or zinc oxide produced *in situ* by adding sodium hydroxide) to form $2ZnO,3B_2O_3,7H_2O$ at room temperature[1021A] or crystalline $2ZnO,3B_2O_3,3{\cdot}5H_2O$ at temperatures above 70°C.[1195, 1199] A solution containing borax, boric acid and zinc chloride at 95°C will precipitate the 3·5-hydrate.[1195, 1199] The 7·5-hydrate has been crystallized in two days from a solution containing zinc sulphate, borax, and boric acid in the molar proportions 1:1:10.[1107A] The 7·5-hydrate is said to be formed by adding boric acid to a zinc salt solution and then adding somewhat more sodium hydroxide than the amount equivalent to the zinc, while the 7·0-hydrate is obtained by adding zinc salt to a borax solution.[481A] A mixture of $K_2B_4O_7$ and zinc sulphate solutions in the molar ratio 3·5:1 gives an amorphous precipitate which crystallizes in 3–4 days to give $K_2O,2ZnO,5B_2O_3,10H_2O$[1107A] (see p. 397). Borax and zinc sulphate solutions give a precipitate which can be converted to $[Zn(NH_3)_3H_2O]B_4O_7,6H_2O$ by treatment with ammonium borate and ammonia solution.[399]

Borax and zirconyl nitrate solutions react to form $ZrO_2,B_2O_3,3H_2O$.[463]

REACTIONS WITH SULPHUR, OXIDES OF CARBON AND PEROXIDES

It has been reported that concentrated borax solution does not react with sulphur[739] but that dilute solutions dissolve small amounts[738] and become greenish-yellow, forming sulphide, polysulphide and thiosulphate as shown by iodine titration.[739] Colloidal sulphur dissolves in borax solutions.[735]

Carbon dioxide is absorbed by solutions of $K_2B_4O_7$[959, 970A, 961]; $K_2B_4O_7$–KCl[959] $K_2B_4O_7$–KB_5O_8–Na_2CO_3[961]; borax–KCl–KB_5O_8–Na_2CO_3[961]; or borax–KCl[960, 962, 970A]; crystalline $KB_5O_8,4H_2O$[962] is formed, or a mixture of $KB_5O_8,4H_2O$ and sodium bicarbonate.[960] The carbon dioxide may be liberated by heating to 100°C.[970A] A solution containing 31·0 g of $K_2B_4O_7,4H_2O$, 4·3 g of $KB_5O_8,4H_2O$ (saturated) and 24·1 g of potassium bicarbonate in 100 ml of water has a vapour pressure of 64 mm at 30°C and 77 mm at 35°C.[961] Sodium borates in methanol react with carbon monoxide to form sodium formate and methyl borate.[1127–8] Borax reacts with carbon dioxide in methanol to give sodium bicarbonate and methyl borate.[1148] Potassium pentaborate solution with added sodium bicarbonate, carbonate or hydroxide, after boiling to eliminate carbon dioxide, forms borax and $K_2B_4O_7,4H_2O$. These can be crystallized separately.[964]

Borax solution reacts with sodium hydroxide and hydrogen peroxide at $-2°$ to 12°C to crystallize sodium perborate.[825] Sodium metaborate solution, added to a hydrogen peroxide solution at 10°–15°C in such a way that the molar ratio $H_2O_2{:}NaBO_2$ is between 1·1 and 1·8, gives sodium perborate with an apparent specific gravity of 0·25–0·45 g ml^{-1}. Increasing the molar ratio gives a lower density.[1010]

Conditions have been found for producing a pourable, abrasion-resistant product.[1010A] A better yield and a higher-purity product are obtained by continuous mixing of sodium metaborate solution with hydrogen peroxide solution containing cadmium sulphate.[981A] When a solution containing sodium metaborate and hydrogen peroxide is passed upward in a column to which fine sodium perborate crystals are continuously fed at the top, and kept in suspension by the upward current, the crystals agglomerate to form larger particles.[1036] Agglomerates having an average bulk density of 0·3–0·6 g ml^{-1} have been prepared.[1002A] The solution, containing magnesium chloride as a stabilizer, may be spray-dried to give sodium perborate having a small particle size.[992A]

Sodium metaborate in the presence of small amounts of water reacts with hydrogen peroxide in an organic medium.[952A] Sodium perborate also may be prepared by oxidizing a hydroquinone in the presence of sodium metaborate.[1182] The effect of borate on the manganese-complex catalyzed decomposition of peroxide has been studied.[816A]

ELECTRODE REACTIONS AND ELECTROLYSIS

Perborates can also be made by electrolysis. In the electrolytic formation of peroxides at various anodes in borax–soda solution, current efficiencies indicate that the process is first order.[398] In perborate formation in lithium, sodium and potassium borate solutions with a platinum electrode, the current efficiency and oxidation rate were higher at higher borate and carbonate concentrations.[396] Polarization curves have been studied in systems of borates, carbonates, and mixtures[397] and the mechanism of perborate formation has been discussed.[1133] In the electrolysis of aqueous solutions containing both borax and potash, using platinum lead, nickel or silver anodes, the highest current yields of peroxide were found with platinum anodes.[610A] The effect of various anode metals on the anode potential, current yield and decomposition of the peroxides has been studied in a sodium carbonate–borax solution[398, 398A] and in a potassium carbonate–potassium pentaborate solution.[324] The effect of electrolyte composition and current density on the current efficiency and peroxide concentration has been studied in mixtures of alkali-metal carbonates with boric acid and with alkali tetraborates.[1175] The relation between current efficiency and perborate concentration using a platinum anode has been studied.[920A, 1253]

In the anodic oxidation of aluminium in aqueous borax–boric acid solution, the formation efficiency was independent of current density.[847A] The formation of non-porous anodic films has been investigated.[18A, 1190A, 351A] In the electro-reduction of oxygen in $Na_2B_4O_7$–Na_2CO_3 solution many cathodes were investigated. The amount of polarization depended on the cathode material.[398A] In anodic polarization of zirconium and columbium in sodium metaborate–sodium hydroxide solutions, the potential decreased with increase in current density.[102]

The anode polarization curves of iron in borate buffer solutions show an unexplained second maximum if the carbon content is above 0·01%.[1237] The effect of borax on the electro-reduction of chromate on a dropping mercury electrode has been investigated.[251A, 1236] The anodic behaviour of tin in deaerated borax solutions has been studied.[748] The polarization of a tellurium electrode in borate solutions at a pH of 7–10 has been investigated.[1233]

Boric acid has been prepared by electrolysis of borax solution in the central compartment of a three-compartment cell. The cathode compartment contained dilute sodium hydroxide, and the anode compartment dilute sulphuric acid. These compartments were separated from the central compartment by cationic and ionic permselective membranes, respectively.[1030] By using a two-compartment cell with a cationic permselective membrane, sodium pentaborate[1030A] and boric acid[1189] have been produced from borax.

CORROSION INHIBITION

Borax has been found to be a good aqueous corrosion inhibitor for steel and zinc.[92, 542] In distilled water, 0·2% of borax is adequate to prevent rust. In tap water, 0·5% or more may be necessary, but the amount varies greatly with waters from various sources. Films formed on iron by 0·1N borax solutions have been studied by electron diffraction and found to consist largely of a cubic iron oxide.[542] A study was made of the corrosion of various steels and zirconium alloys in nuclear reactor solutions containing borates.[532] Iron passivation potential in borate solutions has been studied[261A]; it decreases with an increase in pH.[262A]

Studies of the corrosion and passivation of nickel in 0·1N borax have been made.[197] A study of the corrosion inhibition by sodium pentaborate of the (uranium–8% molybdenum alloy)–(mild steel) galvanic couple showed that sodium pentaborate reduced galvanic attack.[500]

Alkali borates inhibit the corrosion of aluminium[231A, 912], copper and brass[231A] in ethylene glycol. In ethanol antifreeze solutions, 2–3% borax, with added polyhydric alcohol to increase its solubility, inhibits the corrosion of aluminium and iron.[998A]

Borax is a constituent of a corrosion and caking inhibitor for sodium chloride[1008A], and the reaction products of sodium borate and hexanetriol[1041A] and of an alkylene glycol and alkali pentaborate[1187] are used as corrosion inhibitors in hydraulic fluids. Sodium metaborate is a component of corrosion-inhibitor compositions for aqueous cooling systems of combustion engines.[1188]

HYDROTHERMAL REACTIONS

The solubility of 3–15 micron particles of quartz in 0·01M borax solution at 60°C is $4{\cdot}42 \times 10^{-4}$; 70°, $5{\cdot}79 \times 10^{-4}$; 80°, $7{\cdot}15 \times 10^{-4}$; 90°, $9{\cdot}06 \times 10^{-4}$; 100°, $10{\cdot}89 \times 10^{-4}$ moles kg^{-1}.[868, 1134] At 200°–320°C at 60 atm, borax solution will dissolve silica and crystallize quartz on a seed crystal maintained in a cooler zone.[261, 512]

At 328° to 515°C borax solutions dissolve corundum. The effect of temperature, pressure and borax concentration on the solubility has been measured.[498] Borax and boric acid solutions have been investigated for the hydrothermal crystallization of lead titanate, $PbTiO_3$.[769]

At 175° to 275°C borax solution reacts with calcined lithium-bearing silicates to produce dilithium tetraborate in solution.[153, 973]

EFFECT OF BORATES ON CRYSTALLIZATION OF OTHER SALTS

In the non-agitated crystallization of $MgSO_4,7H_2O$ by cooling, addition of 2% of borax decreased the yield to 29 g, compared with 122 g without borax.[800] Borax retarded the growth of crystal faces and shortened the *z*-axis. Borax and sodium hydroxide together shortened it still more.[67] The activation energy of the adsorption of borax on the tetrahedral faces of $MgSO_4,7H_2O$ has been calculated.[94] A systematic study of the effect of borax concentration on the growth of $MgSO_4,7H_2O$ has been made. The crystal habit was changed by 1% of borax from the usual prismatic to the tetrahedral habit. The tetrahedral faces possess the highest adsorption power.[578]

Borax also decreases the crystallization yield of Glauber's salt[800], and retards the growth of Rochelle salt crystals on the [210] surfaces.[68] Low concentrations of borax either increased or did not affect the growth of various faces of potassium aluminium alum, but the growth rate of the [111], [100] and [110] faces decreased sharply as the borax concentration increased above 20 g of $Na_2B_4O_7$ per litre, and became constant at higher concentrations. The growth rate of the [221] and [211] faces decreased uniformly with an increase in borax concentration.[69] The mechanism of the effect has been discussed.[655]

Borax caused sodium chloride to crystallize in dendritic form, but it was less effective than several other salts investigated.[189] Lithium borate caused lithium sulphate to crystallize in dendrites.[189] The effect of borax on the rate of dissolution of anhydrous calcium sulphate has been studied.[470]

REMOVAL OF BORATES FROM SOLUTIONS

Borates are extracted from alkaline brines by contacting with a solution of certain polyol chelating agents in an organic solvent such as kerosene. A preferred chelating agent is 2-chloro-4-(1,1,3,3-tetramethylbutyl-6-methylolphenol.[154, 970] At a pH of 3–7 a mixture of organic diols and alkyl ammonium salts has been used.[996] The borate–diol chelate anion and the alkali cation dissolve in the organic liquid, which is then treated with dilute sulphuric acid to extract boric acid.[150, 154, 416, 968, 970] Borates can also be extracted from dilute brines acidified to a pH of less than about 1·7, with a water-immiscible β-aliphatic diol dissolved in an organic solvent. In this case the borate is extracted from the organic phase by washing with an alkaline solution.[1202] Concentrated magnesium chloride brines have been extracted at pH 2–6 with certain aliphatic diols or catechols to remove borate values.[997] A mixture of diols with five or six carbon atoms in an organic solvent has been used[832A], also 7- to 12-carbon monohydric alcohols in a hydrocarbon solvent.[1024A]

Borate can be precipitated with a mixture of lime and magnesia.[981] When seawater, which contains 4·6 p.p.m. of boron in the form of borate, is treated with just enough lime to precipitate all of the magnesium as the hydroxide, practically all the borate is adsorbed on the precipitate. When an excess of lime is used, the borate is not adsorbed (ref. 1108, 2nd ed., vol. 12, p. 670). A method of producing two grades of magnesium hydroxide, with high and low borate content, from seawater, has been patented.[998] In this method, magnesium hydroxide containing adsorbed borate is precipitated from a stream of seawater. The precipitate is used to adsorb borate from a second stream of seawater. The hydroxide precipitated from the second stream is then low in borate.[998] The adsorption of borate by magnesium oxide has been investigated.[768A, 1012] Fine particles of magnesium oxide are more effective.[767] Basic magnesium chloride adsorbs more borate from solution than does the hydroxide.[768] To remove borate from natural brines containing 0·05–0·2% of boric oxide, a mixture of lime and aluminium or ferric sulphate or ferric chloride is added. Polyacrylamide improves the precipitation. The precipitated hydroxides contain 70–80% of the borate. After washing, the precipitate is treated with sulphuric acid or ferric sulphate to dissolve the borate. The borate is then precipitated in 1–2 h by adding milk of lime to a pH of 8·2.[1014]

The borax concentration in sodium nitrate may be reduced from 0·2% to as low as 50 p.p.m. by dissolving, precipitating with a mixture of magnesia and lime, heating for several hours, filtering and crystallizing.[981]

A calcium borate concentrate has been produced by treating brines, containing magnesium and borate, with lime water.[1012] A calcium–sodium chloride brine, containing 0·2% of boric oxide, has been treated with milk of lime and phosphoric acid to recover the boric oxide content. The precipitate, treated with sulphuric acid, gives calcium borate and phosphoric acid.[1013]

Borates can also be recovered from dilute solutions, at a pH above 4 and preferably about 7, by forming a borate complex on a solid insoluble resinous polysaccharide. The polysaccharide is regenerated, forming boric acid, by means of a dilute acid.[1040A] A process has been patented in which a dilute sodium borate solution is passed through a column of granules of the calcium salt of humic or lignin acid, forming calcium borate in the granules. This calcium borate is then dissolved with steam.[948] Sodium metaborate is selectively adsorbed from borax solution by granules of corn, rice and potato starch.[475]

Borates are adsorbed by clay. When added to some soils, borates are not easy to remove completely.[46] The retention of borate by clay minerals has been studied as a function of pH. Iron and aluminium compounds appeared to be responsible for borate retention. Different clays had different retention characteristics.[775] The adsorption of borate by the clay fraction from a calcareous soil was at a minimum at pH 5·2.[45, 47] Adsorption on kaolinite increased as the pH changed from 3 to 9.[45]

Hydrated iron oxide adsorbed slightly more borate when the pH was increased from 6·3 to 8·23.[45] Borates are adsorbed from solution by zinc and calcium glauconite.[509] Bone charcoal adsorbs boric acid from borax solutions more strongly than it adsorbs the borate ion.[350] Borates are adsorbed from concentrated magnesium chloride brines, in 30 min of contact at room temperature, by powdered alumina which has been activated at 400°–500°C. In one case, 91% of the original boron was removed, leaving a concentration of 31 mg litre^{-1} in the filtrate.[1041] Co-precipitation of borate with the hydroxides of aluminium, iron, tin, manganese and titanium reaches a maximum at pH 7 to 9.[592A, 914, 1092] Boron at 2 p.p.m. is largely precipitated by a mixture of aluminium and calcium chlorides at pH 8 or by calcium chloride and sodium silicate at pH 7.[1056]

Borax in low concentration (about 1%) in a brine is largely precipitated by reaction with dihydroxynaphthalene, leaving about 0·3% of borax in the filtrate.[954]

Borax has been removed from solution by means of a permeable cell.[995]

Practically all borate can be removed from salt solutions, containing for example 11 p.p.m. of boron, by means of Amberlite XE-243 ion-exchange resin.[209A, 464A, 1229] This resin has been investigated for use with irrigation water.[1146A, 1172] Extraction of borate from concentrated brines at pH 7·2[383A], and from a variety of solutions[621A, 740], by a number of ion-exchange resins has been studied. An ion-exchange resin based upon *N*-methylglucamine has a unique specificity for borate.[464]

When borate ions and silicate ions are adsorbed on a column of strongly basic ion-exchange resin, elution with 0·03N and 0·3N-NaOH gives almost complete separation of borate from silicate.[802]

The adsorption of borate from borax–boric acid solutions on Amberlite IRA-400 and -410 bicarbonate-type and chloride-type resins has been studied.[924] Other resinous adsorbents selective for borate and other oxyanions have been patented.[994] A styrene–divinylbenzene resin containing sorbityl groups has been used[1193] to recover borates from brine. The borates are removed from this resin by eluting with water.

REMOVAL OF IMPURITIES FROM BORATE SOLUTIONS

Small amounts of manganese, iron, copper and cobalt may be removed from sodium metaborate solutions by adding a chelating agent such as 8-hydroxyquinoline and filtering, or by passing the solution through a chelating ion-exchange resin, preferably in the presence of a reducing agent such as sodium sulphide or dithionite.[1017]

Iron may be partially removed from sodium borate solutions by adding a zinc salt and a carbonate. The precipitate carries down iron.[1044] In a solution containing 15 p.p.m. of sulphide, the iron content can be decreased by electrolysis to precipitate iron and iron sulphide.[1066] Iron in sodium metaborate solutions may be removed by adding a small amount of calcined magnesia to the hot solution and filtering.[1068] Boric acid may be purified by converting it to sodium pentaborate solution by adding sodium hydroxide or borax, filtering the boiling solution, crystallizing sodium pentaborate, dissolving it and converting it to boric acid again.[1191]

PHASE EQUILIBRIA IN AQUEOUS BORATE SYSTEMS

The crystal growth of some of the less familiar hydrated borates such as Suhr's borate ($Na_2O,5{\cdot}1B_2O_3,7H_2O$), Auger's borate ($Na_2O,5B_2O_3,5H_2O$), disodium enneaborate 11-hydrate ($2Na_2O,9B_2O_3,11H_2O$) and kernite ($Na_2B_4O_7,4H_2O$), is quite slow even when seed crystals are present, and spontaneous seeding may not occur. The crystallization of some of the borates may therefore be disregarded unless their supersaturated solutions are to be kept for appreciable lengths of time.

A review of phase equilibria in aqueous borate systems, including some previously unpublished work, appeared in 1964.[1082] Other compilations are those of Teeple[1116A] and Seidell[1120A], which includes most of the systems in Teeple. Published work on aqueous phase equilibria involving the alkali metal borates is summarized below.

Li_2O–B_2O_3–H_2O, see p. 344.
$LiBO_2$–H_2O, see p. 344.

$Li_2B_4O_7{-}H_2O$, see p. 346–7.

$LiB_5O_8{-}H_2O$, see p. 347–8.

$Li_2B_4O_7{-}LiCl{-}H_2O$. Solubility isotherms at 30° and 80°C were interpreted as indicating that $Li_2B_4O_7,4H_2O$ was the stable borate phase at 30°C and that $Li_2B_4O_7,3H_2O$ was the stable borate at 80°C.[108, 702] However, in a later study of this system, the solid borate phase was identified as $Li_2B_4O_7,3H_2O$ at 25°C.[493]

$Li_2B_4O_7{-}K_2B_4O_7{-}H_2O$. The solid phases are $Li_2B_4O_7,3H_2O$ and $K_2B_4O_7,4H_2O$. A solution saturated with both of these salts at 25°C contains 2·38% of $Li_2B_4O_7$ and 14·15% of $K_2B_4O_7$.[493]

$Li_2B_4O_7{-}K_2B_4O_7{-}LiCl{-}KCl{-}H_2O$.[493] No binary salts or solid solutions were found in a study of the solubility isotherms of this system at 25°C. Solid phases are KCl, $K_2B_4O_7,4H_2O$, $Li_2B_4O_7,3H_2O$ and $LiCl,H_2O$.[493]

$Na_2O{-}B_2O_3{-}H_2O$[281A, 619, 619A, 731, 732, 708, 705, 711, 957, 1082, 1120A], see pp. 353–7.

$NaBO_2{-}H_2O$[619, 1120A], see pp. 358–61.

$Na_2B_4O_7{-}H_2O$[619, 1120A], see pp. 359, 361–6.

$NaB_5O_8{-}H_2O$[619, 1120A], see pp. 359, 375–8.

$NaBO_2{-}NaBO_3{-}H_2O$. Solubility was determined at 18°–50°C.[867] A double salt, $NaBO_2,NaBO_3,4H_2O$, m.p. 88°C, is stable above 18°C. It is orthorhombic and its unit-cell data have been determined.[867]

$Na_2O{-}B_2O_3{-}NaF{-}H_2O$. Solubility and pH determinations were made at 25°C, and solubility diagrams were drawn for the systems $Na_2B_4O_7{-}NaF{-}H_2O$ and $NaBO_2{-}NaF{-}H_2O$ from 70° to 200°F.[407]

$Na_2B_4O_7{-}NaF{-}H_2O$. In a solubility study at 25°C, no complexes were observed.[716]

$NaBO_2{-}HBO_2{-}NaF{-}HF{-}H_2O$. The phase diagram at 30°C shows the areas of borax, sodium fluoride, sodium pentaborate, and sodium metaborate.[606] The formula $Na_2B_2O_4,3H_2O$ given in this paper is apparently a misprint for $Na_2B_2O_4,8H_2O$.

$Na_2O{-}B_2O_3{-}NaCl{-}H_2O$.[488, 1082, 1116A]

$Na_2B_4O_7{-}NaCl{-}H_2O$.[283A, 510, 1082, 1079]

$NaB_5O_8{-}NaCl{-}H_2O$. The 20°, 35°, 70°, 80°, 93° and 100°C isotherms have been determined.[645, 1116A, 1120A] The ternary eutectic is at −22·7°C.

$Na_2B_4O_7{-}H_3BO_3{-}NaCl{-}H_2O$ at 35°C.[957]

$Na_2B_2O_4{-}Na_2B_{10}O_{16}{-}NaCl{-}NH_4Cl{-}NH_3{-}H_2O$.[1082]

$Na_2B_2O_4{-}NaClO_3{-}H_2O$. Solubilities and specific gravities of the solutions were determined between −5° and 75°C. No double salt was formed.[618]

$Na_2O{-}B_2O_3{-}NaClO_3{-}H_2O$.[977] Solubility isotherms at 5° and 20°C for boric acid, sodium pentaborate and borax in this system between the $Na_2O:B_2O_3$ molar ratios 0·15 and 0·25 have been determined in the presence of 5 g of sodium chlorate per 100 g of liquid water used to make up the solution. The solubility peak is decreased and shifted to more acidic solutions in the presence of sodium chlorate.

$Na_2B_4O_7{-}Na_2SO_4{-}H_2O$.[1120A]

$Na_2B_4O_7{-}B_2O_3{-}Na_2SO_4{-}H_2O$ at 20·5°, 23·5°, 28·5° and 35°C.[1116A]

$Na_2O,2B_2O_3{-}NaCl{-}MgSO_4{-}H_2O$.[766]

$Na_2O{-}B_2O_3{-}CO_2{-}H_2O$.[1120A]

$Na_2B_4O_7{-}NaHCO_3{-}Na_2CO_3{-}H_2O$. Phase diagrams have been given for 25° and 50°C.[32, 63] Univariant points are:

Temperature, °C	Liquid composition, wt-%			Solid phases
	Na_2O	B_2O_3	CO_2	
25	14·64	1·63	10·04	$Na_2CO_3,10H_2O$, borax, trona
25	12·79	1·38	9·35	$NaHCO_3$, borax, trona
50	17·72	6·43	10·08	Na_2CO_3,H_2O, borax, trona
50	13·10	3·96	9·33	$NaHCO_3$, borax, trona

$Na_2B_4O_7{-}Na_2CO_3{-}H_2O$. This system was investigated at 35°[328, 1120A], 30°, 35°, 55°, 60°[859] and at 25° and 50°C.[63] At 25°C the liquor composition in equilibrium with both sodium carbonate and borax contains 2·50 wt-% of $Na_2B_4O_7$, and 23·69 wt-% of Na_2CO_3. Above 20% Na_2CO_3 at 35°C, the system becomes quaternary, as trona, $Na_2CO_3,NaHCO_3,2H_2O$, crystallizes.[328]

$Na_2O,2B_2O_3$–$NaHCO_3$–$NaCl$–H_2O.[1116A]

Na_2O,B_2O_3–$NaCO_3$–$NaCl$–H_2O.[1116A]

$Na_2B_4O_7$–$Na_2B_2O_4$–Na_2CO_3–$NaHCO_3$–H_2O.[1116A]

$Na_2B_4O_7$–$Na_2B_2O_4$–Na_2CO_3–$NaHCO_3$–$NaCl$–H_2O.[1116A]

$Na_2B_4O_7$–$Na_5P_3O_{10}$–H_2O. The solubility of borax in $Na_5P_3O_{10}$ solutions at 30°C decreases from 3·23% $Na_2B_4O_7$ at 1·29% $Na_5P_3O_{10}$ to 1·91% in a saturated $Na_5P_3O_{10}$ solution (13·58% $Na_5P_3O_{10}$).[293]

$Na_2B_4O_7$–Na_3PO_4–H_2O.[1196A]

$Na_2B_4O_7$–Na_2HPO_4–$NaCl$–H_2O.[1116A]

$Na_2B_2O_4$–Na_3PO_4–$NaCl$–H_2O.[1116A]

$Na_2B_4O_7$–$Na_2B_2O_4$–Na_2HPO_4–Na_3PO_4–H_2O.[1116A]

$Na_2B_4O_7$–$Na_2B_2O_4$–Na_2HPO_4–Na_3PO_4–$NaCl$–H_2O.[1116A]

$Na_2B_4O_7$–$NaHCO_3$–Na_2HPO_4–$NaCl$–H_2O.[1116A]

$Na_2B_4O_7$–$Na_2B_2O_4$–Na_2HPO_4–Na_3PO_4–$NaHCO_3$–Na_2CO_3–$NaCl$–H_2O.[1116A]

Na_2O–$(NH_4)_2O$–B_2O_3–H_2O.[711]

Na_2O–CaO–B_2O_3–H_2O. The solid phases in this system at equilibrium at 25°C are H_3BO_3, $CaB_6O_{10},4H_2O$, $2CaO,3B_2O_3,13H_2O$ (inyoite), $CaB_2O_4,6H_2O$, $Ca(OH)_2$, $NaB_5O_8,5H_2O$, $Na_2O,2CaO,5B_2O_3,16H_2O$ (ulexite), $NaBO_2,4H_2O$ and borax.[466, 466A, 467] The sodium oxide and boric oxide concentrations at which amorphous calcium borate will crystallize to form $CaB_2O_4,4H_2O$, $CaB_2O_4,6H_2O$, ulexite and inyoite have been determined at 25°C.[281A] The maximum solubility of calcined ulexite occurs when the calcining temperature is 200°–500°C.[1240]

$Na_2B_4O_7$-$Ca_2B_6O_{11}$–H_2O. A schematic diagram showing the phase relations in this system, based on geological occurrence and equilibria between borax, ulexite, and colemanite, has been published.[312]

Na_2O–B_2O_3–SrO–H_2O. An outline of this system has been published.[282]

$Na_2B_4O_7$–Sb_2S_3–H_2O and $NaBO_2$–Sb_2S_3–H_2O. The solubility of stibnite, Sb_2S_3, has been measured in borax solutions containing 1·1 to 3·5% of $Na_2B_4O_7$ at temperatures 100°–250°C and pressures 100–1500 bars.[670A] The solubility increases rapidly with temperature and increases at a decreasing rate with increasing borax concentration, but decreases with increasing pressure. The solubility also increases with alkalinity. In sodium metaborate solution at 100 bars pressure stibnite solubility increases at an increasing rate with rising temperature.[670A] Orpiment and realgar are also appreciably soluble in borax solutions, orpiment reaching 10 millimoles of As_2S_3 and realgar 0·6 millimoles of AsS per kg of solution containing 105·5 millimoles of $Na_2B_4O_7$ at 51°C. Orpiment solubility increased with increased temperature and borax concentration and with decreased particle size.[670A]

$Na_2B_4O_7$–soap–H_2O. The effect of borax on the solubility of soap and the transition temperature from crystalline to liquid crystalline soap has been determined.[565]

Na_2O–B_2O_3–tartaric acid–H_2O. Compounds $3Na_2O,B_2O_3,2C_4H_4O_6,10H_2O$ and $5Na_2O,B_2O_3,4C_4H_4O_6,12H_2O$ were crystallized. High viscosity, specific gravity, and conductivity were found at pH values near 4, along the lines of cocrystallization of sodium pentaborate–bitartrate and boric acid–tartaric acid.[810]

NaB_5O_8–Na bitartrate–H_2O. Addition of pentaborate greatly increases the solubility of the bitartrate. The density, conductivity and viscosity were measured.[809]

Na_2O–K_2O–B_2O_3–H_2O.[711, 1082]

$Na_2B_4O_7$–KCl–H_2O.[510]

$Na_2B_4O_7$–$K_2B_4O_7$–H_2O.[510, 1082]

$NaBO_2$–KBO_2–H_2O.[1082]

$NaBO_2$–KBO_2–B_2O_3–H_2O.[1082]

NaB_5O_8–KB_5O_8–H_2O.[1082]

NaB_5O_8–KB_5O_8–$NaCl$–KCl–H_2O.[1116A]

Na_2O–K_2O–B_2O_3–CO_2–H_2O.[1082]

$NaBO_2$–KBO_2–B_2O_3–NaCl–KCl–H_2O.[1082]

$Na_2B_4O_7$–$K_2B_4O_7$–NaCl–KCl–H_2O.[1116A]

Na_2O–K_2O–$(NH_4)_2O$–B_2O_3–H_2O.[711]

Na_2O–K_2O–MgO–CaO–B_2O_3–H_2O. Solubilities were studied at 25°–70°C. Seven solid phases were observed.[1094]

$K_2B_4O_7$–KB_5O_8–KCl–H_2O.[1116A]

KBO_2–KCl–H_2O.[1082]

K_2O–B_2O_3–CO_2–H_2O.[1082]

K_2O–B_2O_3–H_2O, see p. 387.

KBO_2–H_2O, see pp. 389–90.

$K_2B_4O_7$–H_2O, see pp. 390–2.

KB_5O_8–H_2O, see pp. 394–6.

K_2O–B_2O_3–KCl–H_2O.[461, 461A, 1082] Adding potassium chloride to the K_2O–B_2O_3–H_2O system decreases the pH and the solubility of the potassium borates. The solid phases at 25°C are boric acid and the 1:5:8, 1:2:4 and 1:1:2·5 (K_2O:B_2O_3:H_2O) compounds.

$K_2B_4O_7$–KCl–H_2O.[493, 510, 1082] A solution saturated with $K_2B_4O_7,4H_2O$ and potassium chloride at 25°C contains 2·90% of $K_2B_4O_7$ and 25·13% of KCl.[493]

K_2O–B_2O_3–KCl–NaCl–H_2O.[1082]

$K_2B_4O_7$–NaCl–H_2O.[510]

$K_2B_4O_7$–NaCl–KCl–H_2O.[510]

K_2O–B_2O_3–NaCl–NH_4Cl–NH_3–H_2O.[1082]

K_2O–B_2O_3–CO_2–H_2O.[1082]

$K_2B_4O_7$–K_2CO_3–H_2O at 30°C.[927]

$K_2B_4O_7$–K_2SO_4–H_2O at 30°C.[927]

$K_2B_4O_7$–K_2SO_4–K_2CO_3–H_2O at 30°C.[927]

K_2O–B_2O_3–NaCl–NH_4Cl–NH_3–H_2O.[1082]

K_2O–$(NH_4)_2O$–B_2O_3–H_2O.[711]

K_2O–MgO–B_2O_3–H_2O at 25°C.[467] Solid phases were $MgO,3B_2O_3,7{\cdot}5H_2O$, $2MgO,3B_2O_3,15H_2O$ (inderite), $K_2B_4O_7,6H_2O$, and magnesium hydroxide. No double salts were formed in this study[467], but in another study, $K_2O,MgO,3B_2O_3,15H_2O$ (p. 396) was formed in several days by adding magnesium sulphate solution to $K_2B_4O_7$ solution.[1107A]

K_2O–CaO–B_2O_3–H_2O. A phase-equilibrium diagram of this system at 25°C showed areas in which $K_2O,CaO,4B_2O_3,12H_2O$, $2CaO,3B_2O_3,13H_2O$, $CaB_2O_4,6H_2O$ and $CaB_2O_4,4H_2O$ will crystallize. The compound $K_2O,CaO,4B_2O_3,12H_2O$ (p. 396) is formed at about 3–6% K_2O and 3–8% B_2O_3, and the calcium metaborates were formed at higher ratios of K_2O to B_2O_3.[281, 281A]

K_2O–SrO–B_2O_3–H_2O. $K_2B_4O_7$ and strontium chloride solutions form the orthorhombic compound $K_2O,SrO,4B_2O_3,14H_2O$[1107A] (p. 396).

KBO_2–urea–H_2O. A solubility diagram at 15°, 25° and 40°C has been published which indicates formation of solid solutions and the compound $KBO_2,(NH_2)_2CO$.[217] The 'residue' method suggested the presence of anhydrous potassium metaborate at 40°C in equilibrium with the solution[217], but this is believed to be incorrect as other studies[841] have indicated that the anhydrous salt appears only above 250°C.

Rb_2O–B_2O_3–H_2O, see p. 400.

$RbBO_2$–H_2O, see p. 400.

$Rb_2B_4O_7$–H_2O, see pp. 401–2.

RbB_5O_8–H_2O, see pp. 402–3.

Cs_2O–B_2O_3–H_2O, see p. 405.

$CsBO_2$–H_2O, see pp. 405–6.

$Cs_2B_4O_7$–H_2O, see pp. 406–7.

CsB_5O_8–H_2O, see pp. 407–8.

ALKALI METAL BORATE MELTS, GLASSES AND VAPOURS

Physical Properties

By fusion of various alkali-metal oxide–boric oxide compositions, liquids are formed which, if high in boric oxide content, can be readily cooled to form glasses. Starting materials may be mixtures of alkali-metal borates, boric acid and/or alkali metal carbonates or hydroxides. Reaction rates and mechanisms have been studied in the systems Na_2O–B_2O_3 and Na_2O–B_2O_3–SiO_2.[287] A study has been made of the process of glass formation in borate systems.[543A] There has been considerable interest in these glasses because of the so-called 'boron anomaly' which refers to the maxima and minima in some of their physical properties, such as viscosity, density, thermal expansion and heat content, with changes in composition.[379, 893–4] Several reviews of borate glasses have been published.[254, 447, 517, 858A, 1078, 1110, 1111]

STRUCTURE OF BORATE GLASSES

The curves for viscosity and other properties of alkali borate glasses as a function of composition have been explained from a structural point of view by Biscoe and Warren and others, on the basis of density, thermal expansion and *X*-ray diffraction studies of Na_2O–B_2O_3 and K_2O–B_2O_3 glasses.[61A, 62, 90, 238, 290, 342, 473, 505, 508, 570A, 752, 893–4, 928, 1169] A review on boron coordination in such systems was published in 1962.[446] Boric oxide glass consists of BO_3 triangles, and silica glass consists of SiO_4 tetrahedra. In these glasses each oxygen atom is joined to two silicon or boron atoms to form a continuous network. When alkali-metal oxide is added, the new oxygen atom enters this network. It can do this by breaking a Si–O or B–O bond and forming a bond with the silicon or boron atom, thus forming two non-bridging oxygen atoms, each with one negative charge, and attached to the network by only one bond. This structure would weaken the network and decrease the viscosity. In the case of boric oxide the oxygen atom of the added alkali-metal oxide can also enter the network by bridging between two boron atoms to form two tetrahedral BO_4 groups. This would strengthen the network and increase the viscosity. The shapes of the viscosity composition curves can be accounted for if it is assumed that the relative number of new BO_4 groups formed by addition of alkali is less at high alkali-contents and at high temperatures. At low temperatures, addition of small amounts of alkali metal oxide to boric oxide increases the viscosity[752], hardness, and density[753], and decreases the electrical conductivity and expansivity[753], since the formation of BO_4 groups predominates over the formation of non-bridging oxygen atoms and thus gives a tighter structure. At somewhat higher temperatures, 700°–800°C, the addition of small amounts of alkali oxide forms non-bridging oxygen atoms, decreasing the viscosity. As larger amounts of alkali metal oxides are added, enough BO_4 groups are formed to overcome the weakening effect of the non-bridging oxygen atoms and increase the viscosity. As the mole-% of alkali-metal oxide increases above 33, there is probably a change of these boron atoms back to threefold coordination. *X*-Ray studies have indicated that in lithium borate glasses containing 18 and 50 mole-% of Li_2O, the boron atoms are largely in threefold coordination with oxygen.[441] The sodium and potassium metaborate glasses cannot be made because of devitrification, but in the corresponding crystalline compounds all the boron atoms are in threefold coordination.

An interpretation of the viscosity data for Na_2O–B_2O_3 glasses, based on the increase in the free energy of activation of viscous flow and refractoriness, agreed with this change from three to four in coordination number. This study also suggested that the compounds $Na_2O,3B_2O_3$ and Na_2O,B_2O_3 are formed in the vitreous state and that the bonds in the BO_4 tetrahedra are not equivalent.[551]

In K_2O–B_2O_3 glasses, *X*-ray diffraction patterns indicated a change from three- to four-fold coordination as the K_2O content is increased to 22%.[290]

X-Ray evidence indicates that at room temperature the number of boron atoms tetrahedrally coordinated with oxygen increases with alkali oxide content in glasses containing less than 16·7 mole-% of alkali oxide.[90, 238] This region is sometimes called the accumulation region, and the region above 16·7 mole-% alkali oxide, where non-bridging oxygen atoms are formed, the destruction region.[238] Formulae have been given for the number of non-bridging and bridging oxygen atoms per boron triangle or tetrahedron in these regions[238], indicating that there should be two critical compositions in borate glasses, at 16·7 and 28·6 mole-% of alkali oxide.[238] A break in the conductivity curve at about 28 mole-% alkali oxide has been observed.[759A]

Thermal expansion, viscosity and electrical resistivity studies of various alkali and alkaline-earth borate glasses have indicated that as the atomic ratio of oxygen to boron approaches 2·0, the structure can be represented as consisting of BO_3 chains which are occasionally cross-linked. This model is in agreement with the theories of Zachariasen and of Biscoe and Warren.[473] Volume expansion studies also suggest that as alkali oxide is added, formation of four-coordinated boron predominates below 18 mole-% alkali oxide and formation of non-bridging oxygens predominates at higher alkali concentrations.[504]

Warren[894] showed that at compositions between 0 and 13 mole-% Na_2O, addition of sodium oxide to boric oxide had the same effect in decreasing the thermal expansion coefficient as addition of silica to boric oxide, when compositions were expressed in terms of the average coordination number, assuming the change of as many borons as possible to tetrahedral coordination rather than the formation of non-bridging oxygens. Above 13 mole-% Na_2O, however, the expansion coefficient of Na_2O–B_2O_3 glass increases with increasing sodium oxide, while that of silica–boric oxide glass continues to decrease. This was ascribed to the formation an increasing number of non-bridging oxygens above 13 mole-% Na_2O.

Equilibria in the molten system Na_2O–B_2O_3–NaCl agree with the formation of BO_4 tetrahedra as sodium oxide is added to boric oxide up to the composition $Na_2O,5B_2O_3$; they also agree with the formation of BO_3 groups at higher sodium oxide concentrations.[1140]

Rules have been proposed for the structure of borate glasses: (1) BO_4 tetrahedra cannot be bound to each other; (2) each BO_3 triangle cannot be bound to more than one BO_4 tetrahedron; and (3) non-bridging oxygen ions occur in BO_3 groups only and not in BO_4 groups.[1, 61A, 62] An improved theory for the structure has been derived, based on rules (1) and (3).[62]

The presence of diborate molecular aggregates in $M_2O,2B_2O_3$ glasses has been inferred from the deviations of the nickel oxide solubility curves from ideality.[80A]

Abe[1] discussed the density, expansion, refractive index, molecular refraction and viscosity of Na_2O–B_2O_3 glasses in terms of the formation of groups consisting of one BO_4 tetrahedron with four BO_3 triangles attached to it. This explanation was revised in terms of the 'structon' theory, a structon being a specified atom in a given environment of neighbouring atoms.[342–3] The structons present in borate polyions and differences in the structure of glasses and crystals have been discussed in terms of this theory.[343]

Infra-red spectra of polymerized borate groups in crystals show some relationship to the spectra of borate glasses, indicating the presence of borate groups in the glass phase.[440, 444–5] Interpretation of these spectra in the light of known crystal structures suggested that boric oxide glass consists of boroxol groups in two interpenetrating networks and that addition of one sodium oxide 'molecule' to boric oxide forms one triborate group and one pentaborate group. At 20 mole-% alkali oxide the structure would then consist mainly of two interpenetrating networks of these groups, which gradually change to diborate groups as the alkali oxide is increased to 33 mole-%.[440]

It was found that high pressure did not affect the boric oxide anomaly[798–9]; thus if the anomaly is caused by a change in boron coordination, high pressure did not produce any significant change in the boron coordination number. K_2O–B_2O_3 glasses densified under 25 kilobars had the same fraction of boron atoms in four-coordination as in the original glasses, according to n.m.r. studies.[118]

Vapour pressure studies in the molten Rb_2O–B_2O_3 system[3], showing an $RbBO_2$

activity close to zero at 0 to 16 mole-% Rb_2O, and an increasing $RbBO_2$ activity above 16 mole-%, have been interpreted as indicating that tetrahedrally coordinated boron atoms and bridging boron–oxygen groups are formed below 16 mole-% Rb_2O and non-bridging boron–oxygen groups were formed above 16 mole-% Rb_2O at high temperatures, in agreement with the theory of Biscoe and Warren.[90] At room temperature, however, infra-red studies[1144] indicate no abrupt change at 16 mole-%, but show the formation of tetrahedral BO_4 groups up to at least 33 mole-%, in agreement with the theory of Krogh–Moe.[446, 803] Both vapour-pressure and infra-red data thus agree with the assumption that increasing the temperature decreases the number of tetrahedral groups. Infra-red studies also indicated that the number of BO_4 groups, boroxol groups and $>B{-}O$ groups increases uniformly with Rb_2O content up to 28 mole-% Rb_2O and more rapidly from 28 to 33 mole-%.[1144] Rubidium, sodium and lithium are similar in their effect on the glass structure.[1144] In the Na_2O–B_2O_3 glasses, infra-red spectra showed the maximum concentration of four-coordinated boron atoms at 7 wt-% Na_2O when heat-treated for 2 h at 600°C.[218]

Emission and absorption spectra of Na_2O–B_2O_3 glasses doped with europium suggested two types of centres with different coordination.[208]

Some authors[300–2, 447] hold that in lithium borate glasses, *X*-ray methods are not accurate enough to prove what coordination changes occur, and some *X*-ray studies of these glasses have shown no evidence of four-coordination.[441] At one time the suggestion was made that the change in boron coordination was from four to three, rather than from three to four, when alkali oxide was added to boric oxide.[300–2, 1169] However, n.m.r. studies indicate the formation of BO_4 groups when lithium oxide[688], sodium oxide[117, 290A, 447, 772], or potassium oxide[803] is added to boric oxide in amounts up to 33–45 mole-%. The fraction of the boron atoms which are four-coordinated, as determined by n.m.r. studies, is almost equal to the molar ratio Na_2O/B_2O_3 up to a molar ratio of 0·5, then decreases linearly and becomes zero at a molar ratio of about 2·3.[290A] In K_2O–B_2O_3 glasses also, the fraction of the boron atoms which are four-coordinated is practically equal to the K_2O/B_2O_3 molar ratio up to 0·5 mole of K_2O per mole of B_2O_3.[803] A re-examination of previous n.m.r. studies indicated that in borate glasses, BO_3 groups with one or two non-bridging oxygen atoms can be distinguished from BO_3 groups in which all three oxygens are either bridging or non-bridging.[438A, 339] N.m.r. measurements have been used to determine the fraction of borons which are four-coordinated in relation to composition, and computer-simulated n.m.r. spectra are being used to count the various types of structural units as a function of composition.[438A, 829A, 1171] N.m.r. studies have also been made on cæsium borate glasses and crystalline compounds.[683A, 1091] The formation of BO_4 groups has also been confirmed by *X*-ray methods.[61] The relationship between the fraction of four-coordinated boron and the oxygen coordination has been developed.[290A] A partial molal volume analysis of a 40 mole-% Na_2O plus 60 mole-% B_2O_3 melt has indicated that there are approximately equal numbers of BO_3 and BO_4 groups at 1300°C[686, 687A], in agreement with the n.m.r. results. Methods have also been proposed for calculating the relative numbers of boron atoms in tetrahedral and triangular coordination in borosilicate glasses.[343A] A study of infra-red and n.m.r. spectra indicated the presence of $B_4O_7^{2-}$ groups in Na_2O–B_2O_3 glasses.[771] Structural differences between borate glasses and fibres have been studied by n.m.r.[174]

Other infra-red absorption studies of Na_2O–B_2O_3 glasses indicated that the structure of glasses containing more than 15% of Na_2O was quite different from that of glasses containing 10% or less. Hydrogen bonds were shown to play an important part in the structure of glasses of zero or low soda-content.[16] Infra-red investigations have been interpreted as showing that any water in borate glass is present as OH groups.[579A] The band at 2·95 μ in $Na_2B_4O_7$ glass is attributed to vibrational absorption by OH groups.[313]

There is a good correlation between the infra-red spectra of crystalline and vitreous Na_2O,B_2O_3, $Na_2O,2B_2O_3$, $Na_2O,4B_2O_3$, $Cs_2O,3B_2O_3$ and $Cs_2O,5B_2O_3$.[445] The spectra of cæsium borate and sodium borate glasses are similar, indicating a similarity in the structures.[446]

Infra-red spectra of sodium borate glasses have been interpreted to indicate that there is no single class of coordinated arrangement in the glasses.[100] In Na_2O–B_2O_3 glasses, the infra-red absorption bands change regularly with Na_2O content up to 33 mole-%[103] and indicate a transition from three-coordinated to four-coordinated boron.[127] A similar change was shown for Rb_2O–B_2O_3 glasses.[1144]

The structural groups which occur in crystalline anhydrous borates may also exist in the corresponding glasses. For example, the correspondence between the infra-red spectra of crystalline and glassy anhydrous borax[446], and the small difference between their entropies, suggest that the two-ring B_4O_9 group which exists in borax (and probably exists in anhydrous borax) may also exist in glassy anhydrous borax. Also, the Raman spectrum of borax glass bears some resemblance to that of crystalline anhydrous borax.[322] Similarly the two-ring B_5O_{10} group of potassium pentaborate and the single ring B_3O_8 group of inyoite and meyerhofferite may exist in the borate-glass network.[447] ESR spectra, induced by γ-irradiation, also suggest similar structural groups in $Na_2B_4O_7$ glass and crystals.[1193A]

A consideration of the partial entropies of mixing of borate groups existing in crystalline anhydrous borates, the heats of fusion of $Na_2O,2B_2O_3$ and $Na_2O,4B_2O_3$, and the liquidus curve in the Na_2O–B_2O_3 system, has indicated that $B_3O_{4\cdot5}$, $B_8O_{13}^{2-}$, and $B_4O_7^{2-}$ groups exist in Na_2O–B_2O_3 melts between 5 and 33 mole-% Na_2O.[448] The curves representing the variation of average oxygen volume with composition in alkali-borate glasses show some similarity with the phase equilibrium diagrams, suggesting the presence of chemical combinations in the glasses.[123] Complex borate ions in melts have a greater thermal stability than complex silicate ions.[643]

Other structural explanations of the boron anomaly have been proposed.[447] According to one theory, boron has the ability to vary its coordination number readily between three and four, thus promoting viscous flow.[449] Addition of small amounts of alkali-metal oxide to boric oxide at temperatures below about 500°C would increase the number of polarizable oxygens, making coordination changes less probable and increasing the viscosity.[447] There may also be 'clusters' of the alkali-metal ions.[442–4, 447] Electrical conductivity of molten borates has been discussed on the basis of aggregation of the alkali ions.[449] It has also been proposed that B_4O_6 cage molecules united by dative bonds are present.[633A]

Another suggested explanation of the boric oxide anomaly is that addition of oxide in alkali-metal oxide to boric oxide melts causes binding of boron atoms by hydrogen bonds, thus strengthening the framework.[827] Low-temperature heat-capacity measurements on Na_2O–B_2O_3 glasses, in agreement with acoustical and magnetic studies, were interpreted as indicating that the boric oxide anomaly is due to structural characteristics of the borate network and not merely a change in the coordination number of the boron atoms.[828]

Raman spectra have indicated that BO_3^{3-} ions exist in molten $3Li_2O,B_2O_3$, $2Li_2O,B_2O_3$, $5Li_2O,3B_2O_3$ and $3Li_2O,2B_2O_3$[133], that the ions $B_2O_5^{4-}$, BO_3^{3-} and $B_3O_7^{5-}$ occur in molten $2Li_2O,B_2O_3$[133–4], and that metaborate melts contain high-polymer anions.[134]

Paper chromatography and pH titration studies of aqueous solutions of $NaBO_2$–$NaPO_3$ glasses have been interpreted to indicate that the glasses have chain and branched structures.[608]

Studies of pH using Li_2O–B_2O_3 glass electrodes have indicated that an increase in the Li_2O content up to 42 mole-% causes an increase in the concentration of four-coordinated boron.[96]

X-Ray studies have confirmed that the metal ions in Cs_2O–B_2O_3 glasses are not randomly distributed[442] but appear in pairs.[770]

Tempered Na_2O–B_2O_3 glass has a more open structure than the same glass when annealed.[254] Ultra-violet radiation causes a contraction of an alkali-metal borate glass network.[628]

A structural model has been developed which treats alkali-borate melts as poly-electrolytes with atomically inhomogeneous charge distribution, and which predicts quantitatively their conductivity isotherms.[591] The idea that the liquid state is a dynamic combination of micro-regions has also been applied in detail to silicate and borate melts.[1161]

On the assumption that the entropy of fusion of salts is about 3 g cal per ion formed, molten lithium metaborate would contain more than two ions.[801]

A rapid shift in the absorption edge at about 2000 Å in the composition range 15–20 mole-% M_2O has been attributed to the formation of non-bridging oxygen ions.[547A] Colour-centre studies have indicated that a detectable proportion of non-bridging oxygen ions appears at about 15 mole-% M_2O. A study of absorption spectra indicated that in alkali-borate glasses of high boric oxide content, the proportion of BO_4 groups does not exceed one-fifth of the total number of B–O groups.[579A]

The molar freezing-point lowering of lithium metaborate by excess lithium or boric oxide approaches zero as the concentration of excess oxide approaches zero. This is considered to indicate that molten lithium metaborate dissociates to form $2Li^+ + O^{2-} + B_2O_3$.[936]

A review on boron coordination in alkali-borate glasses was published in 1962.[446] A 1969 review[858A] of the boric oxide anomaly has indicated shortcomings in current theories. A series of papers by Weyl reviews the chemistry and effect of borates in glass technology.[905–9]

STRUCTURE OF MOLTEN SYSTEMS CONTAINING OTHER OXIDES OR SALTS

System $Li_2O–B_2O_3–Al_2O_3$. Two regions having different structures have been identified, based on a study of physical properties.[140]

Systems $NaBO_2$–NaCl *and* $LiBO_2$–NaCl. Experiments on the lowering of the freezing point indicate that sodium metaborate ionizes into more than one particle, and that lithium metaborate and borax ionize into more than two units when dissolved in sodium chloride. This indicates that the borate ions are partially dissociated, probably forming oxygen ions.[314]

Systems $Na_2B_8O_{13}$–KCl *and* –KBr. The lowering of the freezing point of potassium chloride and bromide by dissolved $Na_2B_8O_{13}$ corresponds to 6·8 boron atoms per particle, by dissolved $Na_2B_4O_7$, 3·4; by $NaBO_2$, 1·8; and by Na_3BO_3, 1·05. From the result with $Na_2B_8O_{13}$ it is inferred that although most of the borate ions in this solution have the $B_8O_{13}^{2+}$ formula[574], there are both smaller and larger ions present. The results with the other compounds have been interpreted in terms of borate-ion equilibria.[574]

System $Na_2B_8O_{13}$–KF. The freezing point depression of molten potassium fluoride by dissolved $Na_2B_8O_{13}$ corresponds to 1·7; $Na_2B_4O_7$, 2·5; $NaBO_2$, 1·2; and Na_3BO_3, 1·0 atoms of boron per particle, indicating that $>$B–F bonds are formed.[574]

System $Na_4B_2O_5$–KCl–KF. In KCl–KF melts with a low potassium fluoride content, $2Na_2O,B_2O_3$ gives a freezing point indicating an association between fluoride and borate to give fewer ions than in KCl–KBr melts.[574]

System $Na_2O–B_2O_3$–NaF. N.m.r. investigations have indicated that three types of four-coordinated boron atoms, with BO_2, BO_3F and BO_2F_2 configurations, are present.[414]

System $NaBO_2$–NaF. Freezing-point studies indicated that in fused sodium and lithium metaborates the metaborate ion is somewhat dissociated[649], but later work indicated that it is not dissociated.[746]

System $Li_2O–B_2O_3–SiO_2$. The extent to which silica is polymerized in $Li_2O–B_2O_3–SiO_2$ glasses has been measured. The amount of silica having a low molecular weight, monomer through tetramer, in $Li_2O–B_2O_3$ glasses, was 68–74% of the total silica. When the melt was crystallized this percentage was decreased.[426]

Refs. p. 472

Other systems. Studies of the optical and EPR spectra of nickel oxide in Na_2O–B_2O_3 glasses showed octahedral coordination about the ion sites.[317] Nickel (II) square and tetrahedral species are found in alkali-metal borate glasses when the alkali oxide concentration is 19 mole-% or more.[641]

The absorption spectra of K_2O–B_2O_3 glasses containing small amounts of divalent cobalt have been studied. The Co^{2+} ions change from octahedral to tetrahedral coordination as the $K_2O:B_2O_3$ molar ratio increases from 0·25 to 0·5.[227] The electronic spectra of cobaltous oxide in Na_2O–B_2O_3 glasses indicate a change in symmetry around Co^{2+} with increasing sodium oxide content, owing to increasing ion activity.[573] A series of Na_2O–B_2O_3 glasses containing 0–30% of Na_2O and 0·1% of CoO gave transmission curves indicating a break in the property–composition curves at about 15% Na_2O.[38, 41] An abrupt rate of change of transmission with temperature occurred near the transformation temperature. Potassium borate glasses gave similar results.[38]

Optical spectra of nickel oxide dissolved in $Li_2B_4O_7$, $Na_2B_4O_7$, $K_2B_4O_7$, and $Rb_2B_4O_7$ glasses have been studied and interpreted in terms of the structure.[83]

A theory that alkali metals can assume a covalency of four in glasses has been applied to the effect of boric oxide content on the colour of Na_2O–B_2O_3 glasses and the effects of oxidation and reduction.[178]

Mössbauer, optical absorption and EPR measurements indicate that the co-ordination number of Fe^{3+} in alkali-borate glasses is four at concentrations below 0·05 mole-% Fe_2O_3, whereas at higher concentrations it is predominantly six.[330]

An EPR study of copper in sodium borate glasses has been made.[642A] Optical and ESR spectra of Na_2O–B_2O_3 glasses containing 0·5% of cupric oxide suggest a change in the behaviour of the Cu^{2+} ion in the region of 12 mole-% Na_2O.[319] Electron spin resonance of Fe^{3+}, Cr^{3+} and Mn^{2+} was investigated in Na_2O–B_2O_3 glasses as a function of alkali content.[558] ESR studies of KBO_2–K_2CO_3 compositions are consistent with the identification of the paramagnetic centre as a BO_3^{2-} ion.[830A, 1171]

A study of ultra-violet absorption of pentavalent vanadium in Li_2O–B_2O_3, Na_2O–B_2O_3, and K_2O–B_2O_3 glasses suggests that the vanadate ion changes to a borovanadate ion as the concentration of alkali-metal oxide increases above 24 mole-% K_2O, 26 mole-% Na_2O, or 30 mole-% Li_2O.[641A] Electron paramagnetic resonance and optical spectra have been interpreted in terms of a vanadyl-type structure of fourfold symmetry.[318]

Radiation-induced colouration and infra-red and ultra-violet spectra of alkali-borate glasses containing arsenic trioxide have been used to study structural changes.[91] The cations which have a higher effective field force, and boron, silicon, aluminium and beryllium decrease the oxygen-ion activity and the basicity of a molten glass.[186]

The structures of alkali-metal oxide–B_2O_3–GeO_2 glasses[239A] and of *X*-ray-irradiated Na_2O–ZnO–B_2O_3 glasses[70A] have been studied by electron paramagnetic resonance spectroscopy.[239A] The properties and structure of Li_2O–GeO_2–B_2O_3 glasses have been investigated.[1180–1] Viscosity and density data indicate that in the Na_2O–B_2O_3–GeO_2 system, the BO_4 groups are more stable at high temperatures than was previously thought.[687]

Other studies giving information on the structure of alkali-borate glasses are mentioned in the sections below on viscosity, density and thermal expansion, electrical conductivity, transformation and softening temperatures, compressibility, and optical properties.

VISCOSITY

The viscosity-composition curves for alkali-metal borate glasses have maxima and minima.[231, 336, 489, 491, 505, 508, 613, 752, 883–4, 886, 1166, 1169] The curves for Li_2O–B_2O_3, Na_2O–B_2O_3, and K_2O–B_2O_3 glasses[752] are shown in Fig. 18. At 600°–800°C, a small addition of alkali oxide to boric oxide causes a decrease in viscosity. As more

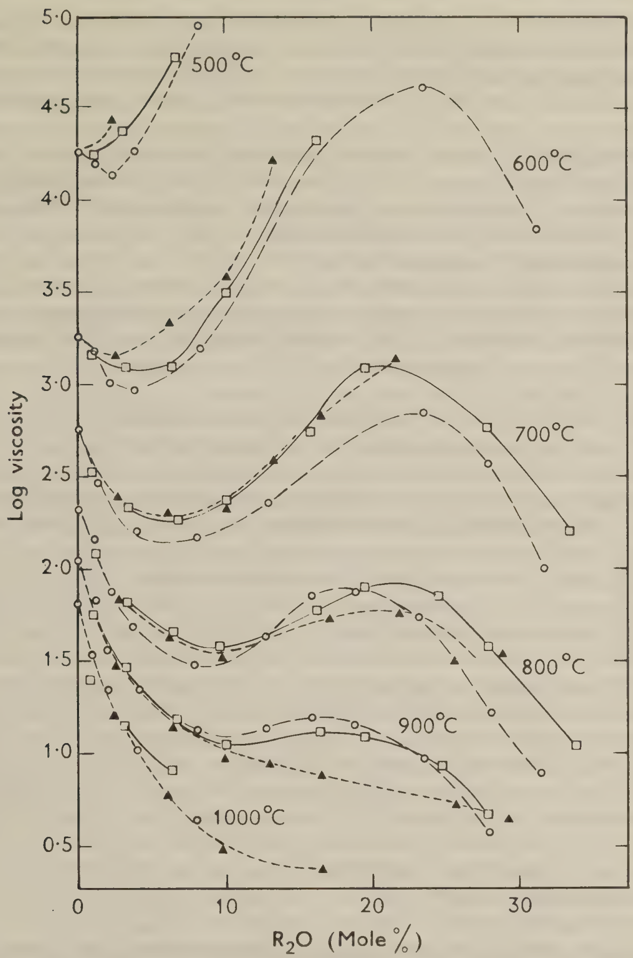

FIG. 18.—Viscosity of alkali borates. Triangles = lithium borates; squares = sodium borates; circles = potassium borates[752]

is added, a maximum viscosity is reached, and when still more is added the viscosity decreases again. Above about 900°C the maximum does not exist, the viscosity decreasing continuously with increase in alkali-oxide content, as is the case with alkali-oxide–silica glasses at all temperatures. The viscosity at 800°–1000°C does not change greatly over a wide range of composition[336] and the initial drop in viscosity disappears at temperatures lower than about 500°C. At temperatures from 200°–350°C the viscosity of K_2O–B_2O_3 glasses increases rapidly from 0 to 20 wt-% K_2O and less rapidly from 20 to 40%. The change in direction of the curves has been attributed to production of non-bridging oxygen atoms.[290] A study of the viscosity of the Na_2O–B_2O_3 system in the softening region indicated that the coordination number changes from three to four.[613] The viscosity of fused borax is 3·3 poises at 880°C and increases to 83,750 poises at 590°C.[887] Below 660°C the viscosity of borax glass is higher than that of boric oxide; above 660°C it is lower.[631] There are two sharp viscosity maxima in the $Na_2B_4O_7$–B_2O_3 system, corresponding to the compounds $Na_2O,3B_2O_3$ and $Na_2O,4B_2O_3$.[883] Explanations of the viscosity curve of melts at temperatures below the liquidus have been questioned because of the possibility of crystallization.[1110]

The viscosity changes with change in composition have been attributed to changes in the boron coordination, as discussed in the section on structure, but other factors also influence the viscosity.[231, 278, 342, 473, 752] The increase in density which occurs when small amounts of alkali-metal oxide are added to boric oxide would have a tendency to increase the viscosity, since there would be less space available for viscous flow.[752]

It has been suggested that the viscosity maximum near the $Na_2O,4B_2O_3$ composition may be due to a high average molecular-weight[1140] or 'degree of aggregation'[231] at this composition. The reduction of viscosity at increased temperature may be to a greater extent due to the lowering of molecular weight by break-up of the polymer than to the coordination change of boron.[1140]

Shear moduli and shear relaxation-times were determined in molten alkali-metal borate by means of ultrasonic velocity and absorption measurements and by using stimulated Brillouin scattering. The results indicated that the relaxation time is the principal cause of the maxima and minima in the viscosity–composition curves.[742A]

The relation between viscosity and free volume has been derived. The data suggest that BO_4 groups (or groups twice that size) are the flow units in alkali-borate glasses, and that the flow units are large in molten boric oxide but decrease with increase in alkali-oxide concentration.[462] Internal friction and thermomechanical curves for two sodium borate glasses have been determined and interpreted in terms of structure.[1198A] The log(viscosity)–reciprocal temperature curves for various B_2O_3–$Na_2B_4O_7$ melts consist of three straight-line sections, the activation energy changing at the points of intersection.[336] Viscosity formulas have been developed which apply to the molten systems $Na_2B_4O_7$–B_2O_3 and $K_2B_4O_7$–B_2O_3.[487] In molten borax there are two regions of viscosity, one above the melting point and the other below it.[487] The activation energy of viscosity[491] in alkali borate melts increases with metal-oxide content up to about 75% M_2O, in contrast to the decrease found in the alkali-metal silicate systems.[1110] Measurements indicate that boric oxide behaves as a Maxwellian liquid, and $Na_2B_4O_7$ glass behaves as a Bingham liquid. The difference in flow behaviour of glassy boric oxide and glassy borax has been explained on the basis of structure.[183A] The rheology of a 8·2 mole-% Na_2O plus 91·8 mole-% B_2O_3 glass showed deviations from Newtonian behaviour.[796]

The influence of tempering Na_2O–B_2O_3 glasses on their viscosity and other properties has been discussed.[254]

Viscosity measurements on molten boric oxide and Na_2O–B_2O_3 at pressures up to 300 bars at 350°–480°C have indicated that activation energies of flow at constant volume are nearly as large as those at constant pressure, suggesting that flow is limited primarily by potential-energy barriers rather than by free volume.[791] Effects of small additions of sodium oxide, water, and sodium fluoride on the viscosity of boric oxide and some binary borates at 380°–470°C at pressures up to 300 bars have been determined.[792] Viscosities of Na_2O–B_2O_3 melts at temperatures up to 600°C under pressures up to 400 bars have been studied.[517A]

A study of the viscosity of $Na_2B_4O_7$–NaH_2PO_4 mixtures at 527°–920°C did not indicate compound formation.[887] In the system $NaBO_2$–$NaPO_3$ a mixture containing 38 wt-% of $NaBO_2$ behaves like a supercooled liquid, and the viscosity increases with temperature. A mixture containing 60% of $NaBO_2$ showed an abnormal viscosity, characteristic of emulsions.[882] An inflection in the 650°C viscosity isotherm coincides with a maximum in the fusion curve at the composition $NaBO_2,NaPO_3$.[883]

The viscosity of $K_2B_4O_7$ containing various amounts of lead oxide and bismuth oxide has been reported. Bismuth gives a higher viscosity than lead.[326]

A study has been made of the effect of dissolved oxides of aluminium, calcium, barium, sodium, and potassium on the viscosity of boric oxide glass.[631]

Viscosities of Na_2O–B_2O_3–SiO_2 melts at 900°–1500°F (482°–798°C)[406], Na_2O–B_2O_3–GeO_2 melts at 600° to 1300°C[687], and of Li_2O–B_2O_3–P_2O_5, Na_2O–B_2O_3–P_2O_5, and K_2O–B_2O_3–P_2O_5 glasses[916] have been investigated.

The viscosity of glasses related to boric oxide has been measured by firing a projectile into the molten glass.[595]

DENSITY AND THERMAL EXPANSION

A review of the physical chemistry of simple molten glasses, including a discussion of density, was published in 1956.[517] The density is increased when small amounts of alkali-metal oxide are added to boric oxide.[517] This density increase is so large that the glass sometimes contains more boron than an equal volume of pure boric oxide. This is true with Na_2O–B_2O_3 glasses up to about 10% of sodium oxide.[753] In Li_2O–B_2O_3 glasses the density increase is greater, and in K_2O–B_2O_3 glasses it is less, than in Na_2O–B_2O_3 glasses. The density–concentration curve in Na_2O–B_2O_3 glasses is S-shaped. At 4% Na_2O there is a widening of the oxygen network.[797] In the alkali-metal borates there are breaks in the curves of the volume of one gram ion of O^{2-}, plotted against the composition, corresponding to various existing and non-existing compounds.[433] The lithium, sodium and potassium borate glasses reach a maximum density at 27 to 33 mole-% alkali-metal oxide.[1169] At high temperatures the maximum density at 600°–1000°C is at about 30 mole-% alkali oxide.[753] There is some difference in the density values reported by various observers for the alkali-metal borate glasses at room temperature.[159, 238, 285, 290, 364, 473, 753, 797] This may be due to variations in the amount of structural water, due to differences in the method of preparation, or it may be due to formation of boric acid on the surface of the glass by absorption of atmospheric moisture.[238] Annealing increases the density of Na_2O–B_2O_3 glasses as compared with the same glasses when quenched.[238] Quenched Na_2O–B_2O_3 glasses which had been melted *in vacuo* had lower densities than quenched glasses melted in air[238], indicating that the density is sensitive to water content. There were breaks in the density–composition curve at about 15 and 26 wt-% Na_2O.[238] The effect of tempering on the specific volume and expansion has been discussed.[254] Proposed methods for calculating densities of glasses from their composition do not apply to binary alkali-borate glasses.[753]

Density determinations on a variety of borate glasses have been used to calculate the apparent molar volume. The apparent molar volume of the lithium borates is less than that of the sodium or potassium borates.[818] Density–composition curves have been published for Na_2O–B_2O_3, K_2O–B_2O_3 and Li_2O–B_2O_3[122, 724], and for Cs_2O–B_2O_3.[454] Density equations have been given[686] and a high-temperature partial molar volume analysis[686] has indicated that at 40 mole-% Na_2O, at 1000°–1300°C, about half of the boron atoms are in four-fold coordination. The specific volumes of molten sodium metaborate ($NaBO_2$) and dipotassium tetraborate ($K_2B_4O_7$) have been determined at temperatures from 1000° to 1250°C. At these temperatures the volumes for sodium metaborate are 0·524 and 0·566, and for dipotassium tetraborate 0·520 and 0·565 respectively.[888] The density and surface tension of molten sodium borate systems has been determined at 1100°C.[1234]

Density–temperature data have been determined for the molten Rb_2O–B_2O_3 and Cs_2O–B_2O_3 systems in the range 500° to 1100°C.[504, 506]

Densities in the molten system $Na_2B_4O_7$–MoO_3 at 600°–1200°C do not follow the rule of additivity.[297]

From an experimental study of the expansion coefficients of the borate glasses of the five alkali metals at $-196°$ to 25°C it was concluded that the expansion coefficient varies with structure in a generally predictable manner.[858A] As sodium oxide is added to boric oxide, the expansion coefficient at 15°C, which is $14{\cdot}3 \times 10^{-6}$ for boric oxide, decreases steeply to a minimum of about $8{\cdot}64 \times 10^{-6}$ at about 85% B_2O_3[1, 719], increases to a maximum of about $11{\cdot}1 \times 10^{-6}$ at 69% B_2O_3, and decreases to $8{\cdot}05 \times 10^{-6}$ at 57·2% B_2O_3.[719] For a glass containing 6·7% of Na_2O and 93·3% of B_2O_3, the expansion coefficient is constant at $9{\cdot}85 \times 10^{-6}$ from 15° to 270°C.[719] It is also constant from 800° to 1200°C in the systems $Na_2B_4O_7$–B_2O_3 and $K_2B_4O_7$–B_2O_3.[490] In the low-alkali region, expansivity decreased with increasing temperature, but in the high-alkali region the opposite was true.[753] Other studies have been reported.[159, 473] The specific volumes of $Na_2B_4O_7$–B_2O_3 melts have been determined at temperatures of 500°–1200°C.[889] The expansion of alkali-metal borate glasses is higher if the glass has been cooled slowly.[742] Tempering and plastic deformation also affect the expansion.[742]

The linear expansion coefficient of Li_2O–B_2O_3 glasses containing 82·4 and 87·5% of B_2O_3 are 9·8 and $11{\cdot}6 \times 10^{-6}$ per deg C.[724] The volume expansion coefficient has been plotted against the composition for melts of Li_2O–B_2O_3[504, 753], Na_2O–B_2O_3[285, 504, 753], K_2O–B_2O_3[504, 753], Rb_2O–B_2O_3[504], and Cs_2O–B_2O_3.[504] At 800°C, when alkali oxide is added to boric oxide, the expansion increases rapidly at first and then remains almost constant until the composition reaches about 18 mole-% of alkali-metal oxide.[504] With a further increase in alkali oxide, the expansion increases rapidly in the order Cs > Rb > K > Na > Li. A suggested explanation of this behaviour is that formation of four-coordinated boron predominates as alkali oxide is added, up to about 18 mole-% alkali oxide, and formation of non-bridging oxygens predominates above that concentration.[504] The expansion coefficient for K_2O–B_2O_3 glass at 200°C also reaches a minimum at 16–20 mole-% K_2O and this has been interpreted similarly.[290] Other studies on K_2O–B_2O_3 glasses have been made.[159] Most Na_2O–B_2O_3 glasses undergo a permanent densification when a high pressure is applied. The percentage densification at 40 kilobars and 250°C decreases with increasing sodium oxide content from 14·2% for boric oxide to 6·3% for borax. At 40 kilobars and 25°C the corresponding changes are 5·6% and 1·4%.[798–9]

Density data have been determined for Na_2O–MgO–B_2O_3[552, 556], Li_2O–MgO–B_2O_3[543, 552, 556], K_2O–MgO–B_2O_3[552, 556], Na_2O–BeO–B_2O_3[554, 556], K_2O–BeO–B_2O_3[555–6], and Li_2O–BeO–B_2O_3[552, 556] glasses, and density and thermal expansion have been measured for Li_2O–B_2O_3–P_2O_5, Na_2O–B_2O_3–P_2O_5, K_2O–B_2O_3–P_2O_5[916], Li_2O–B_2O_3–SiO_2[190, 1163], and Li_2O–B_2O_3–Al_2O_3–SiO_2 glasses.[1251]

System Li_2O–MgO–B_2O_3. Density data (1·91–2·38) show anomalies attributed to the formation of compounds such as magnesium borates in the glass.[543, 552, 556]

System Li_2O–B_2O_3–Al_2O_3. The thermal expansion coefficients of Li_2O–B_2O_3–Al_2O_3 glasses at 20°–400°C were found to agree closely with those calculated from the compositions of the glasses and the thermal expansion of the oxides. Low coefficients were not obtained in this system.[86] Adding alumina to $Li_2O,4B_2O_3$ causes a substantial decrease in the thermal expansion coefficient.[140] Below the transformation region, aluminium reduces the thermal expansion. Above this region, it increases it.[140]

Systems Na_2SiO_3–B_2O_3 *and* $NaBO_2$–SiO_2. The density and thermal expansions of these systems have been determined.[285]

System Na_2O–SiO_2–B_2O_3. The density–composition curves were similar to the refractive index curves.[5A, 1188A]

System Na_2O–B_2O_3–GeO_2. Interpretation of density and viscosity data indicate a fairly broad stability region for BO_4 tetrahedra.[687]

System Na_2O–B_2O_3–PbO. The effect of thermal treatment on the density was determined.[642]

System $NaBO_2$–$NaPO_3$. This system from 600° to 1000°C shows a minimum volume corresponding to the composition $NaBO_2,NaPO_3$.[492]

System $Na_2B_4O_7$–KPO_3. At 650°–1200°C there is a contraction at $Na_2B_4O_7$ concentrations from 16 to 64 mole-%.[492]

System $Na_2O,4{\cdot}5B_2O_3$–As_2O_3. The change in slope of the curves of density against percentage of arsenic trioxide may be related to structural changes.[91]

System Cs_2O–B_2O_3–PbO. The coefficient of linear thermal expansion was determined at 20°–120°C.[87]

THERMAL AND ELECTRICAL CONDUCTIVITY

A review which included a discussion of conductivity was published in 1956.[517]

The thermal conductivity coefficient of molten borax changes almost linearly from 3·24 at 750°C to 4·52 kcal m^{-1} h^{-1} deg C^{-1} at 950°C.[303A]

The electrical conductivity of borax decreased with loss of water as the temperature was increased to 350°C. The conductivity of the resulting amorphous anhydrous borax increased slowly with temperature up to 575°C, where crystallization occurred.[216] The specific electrical conductivity of molten borax is much less than that of salts of most other acids.[623] In a log K *versus* $1/T$ diagram, a straight line connects the points between 660° and 480°C and another straight line connects points at lower temperatures. The two lines intersect at about 480°C.[623] At 270°–300°C the conductance of borax glass is due entirely to the sodium ions, which have a transference number of $1{\cdot}02 \pm 0{\cdot}2$.[633]

Theoretical studies of the conductivity of molten Na_2O–B_2O_3 and Na_2O–SiO_2 glasses have been made.[432] The conductivity–composition curves of the molten Li_2O–B_2O_3, Na_2O–B_2O_3 and K_2O–B_2O_3 systems, determined at 700°–900°C[752], do not show a 'boron anomaly'. The conductivity at 600°–1000°C increases rapidly with alkali content up to five equivalents of alkali per litre and increases less rapidly with further addition in alkali.[752] The conductivity of Na_2O–B_2O_3 glasses[591] at 298°–674°C was found to increase with sodium oxide content.[835] In other experiments, however, at temperatures below 370°C, the conductivity of boric oxide is decreased by addition of small amounts of sodium oxide but increased by addition of larger amounts.[601, 790] There is a sudden increase at 4% Na_2O.[797] A break in the conductivity curve at about 28 mole-% of alkali has been observed.[759A] Discontinuities have been observed at compositions corresponding to compounds.[794] In Na_2O–B_2O_3 and K_2O–B_2O_3 glasses at various temperatures there is a maximum specific conductivity at 20% Na_2O and at 15% K_2O.[408] The conductivity–temperature curves for Na_2O–B_2O_3 glasses show fairly sharp breaks in the region of transition from liquid to glass.[790] Curves have been published showing the resistivity in the Rb_2O–B_2O_3 and Cs_2O–B_2O_3 systems as a function of temperature, and conductivity as a function of alkali concentration.[507] In the molten systems Rb_2O–B_2O_3 and Cs_2O–B_2O_3 at 700°–900°C the conductivity increases very rapidly with alkali content up to one or two equivalents of alkali per litre.[507, 539] Above two equivalents of alkali the conductivity increases at a slower, constant rate with increase in alkali-metal content. This behaviour has been attributed to a change in the structural configuration.[507]

A structural model has been developed which predicts quantitatively the conductivity isotherms of the alkali borates.[591]

There is a parallel between the electrical conductivity and the dielectric properties.[390] Activation energies for conduction in the molten alkali-metal borates have been shown to be almost independent of the size of the alkali-metal ions.[517, 1169] The equivalent conductance increases with electrolyte concentration[592], in contrast to the behaviour of electrolytes in aqueous solution.

The conductivities of Li_2O–B_2O_3, Na_2O–B_2O_3 and K_2O–B_2O_3 melts containing up to 50 mole-% of alkali-metal oxide have been measured and represented by an equation.[592] Theoretical studies have been made.[590] The effect of both temperature and pressure on the conductivity of simple borate glasses as a function of temperature and pressure up to 5000 $\mathrm{lb\ in^{-2}}$ has been measured, indicating that both the activation energy and the activation volume for conduction reached maximum values at temperatures near the glass transition point.[595]

For the molten alkali-metal borates there is a linear relationship between log(resistivity) and log(viscosity).[752] The slope d(log resistivity)/d(log viscosity) varies from 0·8 to 3·0, depending on the nature of the alkali-metal oxide, and increases linearly with alkali-metal oxide content.[1169] The resistivity increases with the volume of the cation.

The conductivity and viscosity of Na_2O–B_2O_3 melts have the same dependence on temperature.[544] At 290°–650°C the temperature coefficient is the same in amorphous and crystalline states.[417]

The conductivity–temperature curves of cooling Na_2O–B_2O_3 melts show a distinct change in slope, which has been attributed to sub-liquidus liquid-phase separation.[890] Other conductivity studies have been published.[433A, 473, 541]

In the Li_2O–K_2O–B_2O_3 and Li_2O–Na_2O–B_2O_3 systems there is a minimum conductivity at equal concentrations of the alkali oxides.[540] This is also true in the Na_2O–K_2O–B_2O_3 system at 100°–300°C.[126] The mobility of the cations was much higher than that of the anions. The transport numbers of Na^+ and K^+ were the same.[523]

System Na_2O–B_2O_3–Ag_2O. Conductivity measurements in this system have indicated that the Ag^+ ion is not bonded to the oxygen ion in the melt, but is free to move in the melt like Li^+, Na^+, and K^+.[424] There is a conductivity minimum at the Ag:Na ratio 1:4.[537]

System K_2O–B_2O_3–Ag_2O. A minimum in the conductivity at 250° and 300°C appears at $Ag:K=1:4$.[536, 538] The conductivity is higher than in the Ag_2O–B_2O_3 and K_2O–B_2O_3 systems at high silver oxide concentrations.[536]

System Na_2O–BaO–B_2O_3. The conductivity due to sodium is decreased by large concentrations of barium oxide.[540]

System Li_2O–B_2O_3–Al_2O_3. The conductivity and its thermal coefficient have been determined for various compositions in this system.[140]

System Li_2O–B_2O_3–SiO_2. The conductivity at 20°C has been determined for various compositions in this system and for related four- and five-component systems.[190]

System $Na_2B_4O_7$–MoO_3. The effect of temperature and composition on the conductivity was investigated.[295]

Systems $Na_2B_4O_7$–$NaCl$ *and* $Na_2B_4O_7$–NaF. The conductivity increases with the concentration of the halogen salt, but the temperature coefficient decreases.[794]

TRANSFORMATION AND SOFTENING TEMPERATURES

The transformation temperature (temperature of inflection of the physical property curves) has been determined in Na_2O–B_2O_3 glasses at various compositions between 0 and 43 wt-% Na_2O. Devitrification prevented studies at higher sodium oxide concentrations. A maximum exists at the composition $Na_2O,2B_2O_3$.[719] The transformation temperature of Na_2O–B_2O_3 glasses, determined as corresponding to a viscosity of $1{\cdot}86 \times 10^{13}$ absolute units, increases from 245° to 410°C almost linearly as the composition is changed from boric oxide to $Na_2O,4B_2O_3$[364–5, 384], increases about 20° more from $Na_2O,4B_2O_3$ to $Na_2O,2B_2O_3$, and then decreases slowly with further addition of sodium oxide.[364–5] Transformation temperatures, as determined by measurement of elastic vibrations of the cooling melt, show maxima of 425°C at 0·153 moles of sodium oxide per mole of boric oxide and 487°C at 0·333 moles of sodium oxide. There was good agreement with results determined by measuring the viscosity.[489]

The softening point of K_2O–B_2O_3 glasses has been determined.[159] Transformation and softening temperatures in K_2O–B_2O_3 glasses increase rapidly as the potassium oxide content increases from 0 to 20 wt-%; as the potassium oxide is increased further, there is a small increase.[290]

The effect of tempering on the transformation temperature has been discussed.[254]

The temperature of maximum damping of mechanical oscillations in alkali-borate glasses is increased by tempering, slow cooling and plastic deformation.[742]

The lowest temperature at which movement of structural units occurs in lithium, sodium, potassium and cæsium borate glasses has been determined by expansion and differential calorimetry experiments. The congealing temperature increases linearly with alkali-metal oxide content. With slowly cooled glasses the congealing temperature is higher during heating than during cooling. In quickly cooled glasses this temperature is the same during heating and cooling.[384]

System Li_2O–B_2O_3–Al_2O_3. The transformation and softening points are at a maximum at a $Li_2O:B_2O_3$ molar ratio of 0·5 and at 0 to 10% of Al_2O_3.[140]

System Li_2O–B_2O_3–SiO_2. Softening temperatures have been determined by interferometry.[1163]

System Li_2O–B_2O_3–Al_2O_3–SiO_2. Deformation temperatures have been reported.[1251]

System Na_2O–B_2O_3–PbO. The devitrification and softening points have been determined.[642]

System Cs_2O–B_2O_3–PbO. Softening temperatures in this system were found to be 120° to 250°C.[87]

SURFACE TENSION

A review including a discussion of surface tension was published in 1956.[517] A tabulation of published surface tension values gives 264·8, 201·6 and 136·6 dynes cm^{-1} for lithium, sodium, and potassium metaborates, respectively at their melting points.[784]

The surface tension of sodium borate systems has been determined at 1100°C.[1234]

As lithium, sodium, potassium, rubidium or cæsium oxide is added to boric oxide at temperatures between 700° and 1200°C, the surface tension increases.[433, 503, 517, 751, 1169] At 900°C, in the case of the potassium borate system, the surface tension reaches a maximum at 30 mole-% K_2O; the other curves probably do also at concentrations higher than those investigated. The cæsium curve reaches a maximum at about 25% Cs_2O.[503] With less than about 15 mole-% of Li_2O, Na_2O or K_2O the temperature coefficient of surface tension is approximately equal to that of boric oxide, which suggests that the surface consists largely of boric oxide. This conclusion is in agreement with the tendency of molten borates to separate into two liquids, one of which is nearly pure boric oxide.[751] In the alkali-metal borates the latter phase can be considered as confined to the surface. The relations among the surface tension, binding energy, crystal lattice-energy and ionic or covalent radii in the series $LiBO_2$–$NaBO_2$–KBO_2 at 1200°C have been discussed.[632]

A study has been made[1160] of the wettability of metals by molten sodium borate ($Na_2O,3B_2O_3$). The contact angle changes over a period of time, indicating that a reaction is taking place. If potassium iodide is added, molten sodium borates do not wet platinum.[919] The surface tension of molten borax is significantly decreased by adding potassium chloride, greatly decreased by potassium fluoride, and only slightly decreased by adding boric oxide.[630A]

The surface tension of $Na_2B_4O_7$–MoO_3 melts has been determined as a function of temperature and composition.[296] Molten lithium metaborate *in vacuo* formed drops on platinum, but when oxygen was present it formed thin films.[232]

The cohesion between freshly fused spheres of borax glass corresponds to a surface energy of 69 ergs cm^{-2}. The cohesion in air is thought to be due to a film of water, since in a vacuum or dry air the cohesion is decreased to about one-third.[115] Molten borax may be blown into a mineral wool which, after coating with a resin, is suitable for neutron shielding and thermal insulation.[949]

HARDNESS

The maximum diamond pyramid hardness in the Na_2O–B_2O_3 system was observed to occur at $Na_2O:B_2O_3$ molar ratio 1:5.[5] In another study, quenched Na_2O–B_2O_3 glasses showed a maximum diamond pyramid hardness at about 25 wt-% Na_2O.[239] With annealed glasses, the hardness values were higher and the highest values were between 17 and 28 wt-% Na_2O. The effect of electron irradiation on the microhardness of simple borate glasses has been studied.[862A] In the system Na_2O–B_2O_3–PbO, the effect of heat treatment on the microhardness has been determined.[642]

ELASTICITY

Young's modulus was determined for $Na_2O–B_2O_3$ and $Na_2O–K_2O–B_2O_3$ glasses.[241–2] A small addition of sodium oxide to boric oxide causes a large increase in Young's modulus.[241] A maximum occurs when the oxygen atom to boron atom ratio is 1·733.[242]

COMPRESSIBILITY

Compressibility decreases with increase in alkali-metal content[897, 1090]; the effect is much greater in borates than in silicates. When potassium borate glasses were subjected to high pressure (*ca* 100,000 bars) the molar volume was reduced by 8%, the refractive index increased by 2·5–3%, the thermal expansion increased by 0–30%, and the molecular refraction decreased by 2%. Infra-red spectra, however, agreed with those of the original glasses.[652] Data on compressibility in molten $Li_2O–B_2O_3$, as measured by sound velocity, agree with the existence of discrete anions at high lithium oxide concentrations.[97]

SOUND VELOCITY

Measurements of the velocity of ultrasound in $Na_2O–B_2O_3$ glasses indicate that the structure becomes stronger as the sodium oxide content increases from 0 to 25 mole-%.[279] The maximum ultrasound velocity is at 25 mole-% Na_2O.[279] The velocity of ultrasound in $Li_2O–B_2O_3$ glasses increases from 3000 to 5000 m sec^{-1} as the lithium oxide content increases from 0 to 22·5 mole-%, indicating that the three-dimensional nature of the structure is increased.[826] Glasses containing lithium have a higher sonic velocity and a smaller compressibility than potassium-containing glasses.[928] Ultrasonic velocity and absorption and stimulated Brillouin scattering studies have indicated that shear relaxation time is the principal cause of the maxima and minima in the viscosity-composition curves.[742A]

STRESS

Ultra-violet radiation causes stress build-up in some borate and borosilicate glasses, owing to contraction in volume in the irradiated surface layers. Some oxides increase and some decrease the build-up, when added in small amounts. Ceric oxide, lead oxide and uranium dioxide in small amounts increase the stress, but in larger amounts decrease it.[410] In another study of many binary borate glasses, stress build-up was observed only in glasses containing lithium, sodium, and potassium.[630] The mechanism[628] and effect of additives[629] have been studied.

DIFFUSION OF METAL IONS

Activation energies for diffusion of cæsium in $Cs_2O–B_2O_3$ glasses, calculated from ^{133}Cs n.m.r. line widths, increase linearly with increasing cæsium oxide content.[683] Diffusion coefficients for heavy-metal ions in fused borax have been investigated.[207] The diffusion of silver ion in molten sodium borate was studied by means of chronopotentiometry.[817A]

MAGNETIC PROPERTIES

Alkali-metal borate glasses are diamagnetic.[121] The specific magnetic susceptibility of (probably amorphous) $Na_2O,5B_2O_3$, dehydrated by heating above 200°C, has been found to be $-0{\cdot}39 \times 10^{-6}$ c.g.s. units.[663] The magnetic susceptibility has been determined for cobaltous and nickel oxides dissolved in borate glass.[121] The susceptibility of borax glass containing cobaltous oxide decreased at first with time, then rose to a maximum and decreased slowly to a constant value.[348] Borax glass containing dissolved ferrous and ferric oxides was paramagnetic, but a relation between degree of oxidation and magnetic susceptibility could not be found. The specimens were ferromagnetic after tempering.[286] Another study has been made of the effect of oxidizing and reducing conditions on the magnetic susceptibility of sodium borate glasses containing iron oxide at 20°–400°C.[40]

Paramagnetic resonance in borax glass containing ^{59}Fe and ordinary iron (at

77 K)[269] and in cæsium borate glasses containing copper[1249], have been measured. The magnetic moments of Co^{2+}, Ni^{2+}, and Cu^{2+} in alkali-borate glasses are dependent on the composition of the alkali borate.[373]

DIELECTRIC PROPERTIES

The dielectric loss of Li_2O–B_2O_3 glasses is higher, and that of K_2O–B_2O_3 glasses is lower, than that of Na_2O–B_2O_3 glasses.[776] The dielectric loss shows a minimum at $Na_2O:B_2O_3$ molar ratios of approximately 0·1[358, 390, 776], and a maximum at 30–50 K.[358] In K_2O–B_2O_3 glasses the maximum loss occurred at approximately 50 K; in Na_2O–B_2O_3 glasses it occurred at 35–45°K.[359] Dielectric losses of borate glasses containing both sodium and potassium indicated that the presence of the two alkali oxides strengthens the glass.[358] Borate glasses containing potassium and lithium showed a minimum in loss angle at a K:Li ratio of 28:42.[390]

OPTICAL PROPERTIES AND SPECTRA

In Li_2O–B_2O_3 glasses the index of refraction increases linearly with lithium oxide content according to one investigation[122], but non-linearly according to another.[724] For Na_2O–B_2O_3[122] and K_2O–B_2O_3[122, 159] glasses, the relationship is complex. Indices of refraction for Na_2O–B_2O_3 glasses at 20°C for sodium light have been tabulated.[364] The index of refraction–composition curve for quenched Na_2O–B_2O_3 glass which had been melted in air shows breaks at about 15 and 26 wt-% Na_2O. The curve for glasses which had been melted *in vacuo* do not show these breaks, indicating that the water content has an appreciable effect on the refractive index.[238] The specific refraction, however, is not much affected by the water content or by quenching or annealing.[238] The index of refraction of a 70% Na_2O–30% B_2O_3 glass increases with temperature up to 420°C, but there are variations from a straight line which are difficult to explain.[922] The difference between the refractive indices of quenched and annealed Na_2O–B_2O_3 glasses reached a maximum at the composition $Na_2O:B_2O_3 = 1:1$, suggesting compound formation. In Na_2O–B_2O_3–SiO_2 glasses this maximum occurred at the composition $Na_2O:B_2O_3:SiO_2 = 1:1:2$.[5A]

Molecular refraction studies have been carried out on water-free Na_2O–B_2O_3 and Na_2O–B_2O_3–NaCl glasses.[923]

Refractive dispersions have been measured on $Na_2O,2B_2O_3$, $Na_2O,4B_2O_3$, and boric oxide glasses.[581] Indices of refraction were measured on Na_2O–B_2O_3 glasses which had been pressed at 40 kilobars at temperatures up to 250°C.[798]

From studies of the orientation double refraction induced by flow in molten boric oxide and in a melt of the composition 5·52 mole-% Na_2O–94·48 mole-% B_2O_3, it was concluded that molten boric oxide consists of small units about 20 to 40 Å in size. Introduction of sodium oxide into boric oxide causes a decrease in the size of these units and decreases the anisotropy.[374]

The optical spectrum of borax glass[317] and the ultra-violet[547A] and infra-red[103, 547] spectra of Na_2O–B_2O_3 glasses have been studied. The wavelength of the ultra-violet absorption edge increased sharply between 15 and 20 mole-% Li_2O or K_2O, indicating a sharp increase in the amount of non-bridging oxygen.[547A]

Induced optical and electron spin resonance spectra were studied in a series of alkali-metal borate[607] and K_2O–B_2O_3 glasses.[32A, 1191A]

The ESR spectra of $Na_2O,4B_2O_3$ glass have been studied after gamma-ray and ultra-violet irradiation.[409] ESR examination of gamma-irradiated Li_2O–B_2O_3 glasses showed a previously unreported structure in the spectrum.[299] As the alkali content of alkali borates is changed, there appears to be a correlation between the change in structure and the formation of magnetic centres by gamma-rays.[1132]

Radiation-induced colour centres in crystalline and amorphous borax have been studied by optical, electron spin resonance, thermoluminescence spectra and thermoluminescence glow curves.[85A] The formation of defects stable at room temperature is more efficient in glasses than in crystals. Radiation-induced colour centres have been correlated with structure in alkali borate glasses, by means of optical and

ESR spectra.[1151] A paramagnetic defect, which may be of use as a probe of the structure of the alkali-metal borate glasses, was observed in ESR studies after *X*-irradiation at cryogenic temperatures.[299A]

Borax glass coloured by exposure to radium does not give a photoelectric current. Its absorption spectrum has a maximum at 545 mμ.[860] The thermoluminescence of gamma-irradiated fused borax has been studied by ESR.[1193A, 85]

Indices of refraction have been measured for glasses in the systems $Li_2O–B_2O_3–P_2O_5$, $Na_2O–B_2O_3–P_2O_5$, $K_2O–B_2O_3–P_2O_5$[916], $Li_2O–MgO–B_2O_3$[552, 556], $Na_2O–MgO–B_2O_3$[552, 556], $K_2O–MgO–B_2O_3$[552, 556], $Li_2O–BeO–B_2O_3$[553, 556], $Na_2O–BeO–B_2O_3$[554, 556], $K_2O–BeO–B_2O_3$[555, 556] and $Na_2O–B_2O_3–SiO_2$.[5A] Substitution of small amounts of boric oxide for silica in $Na_2O–B_2O_3–SiO_2$ glasses increases the index of refraction to a maximum at 20% B_2O_3.[891] Refractive dispersions have been measured in the system $Na_2O–B_2O_3–SiO_2$. Inflections in the dispersion–composition curve were ascribed to compound formation.[1188A] The effect of adding arsenic oxides on the gamma-induced colouration of lithium, sodium and potassium borate glasses has been studied.[91] The system $LiBO_2–Ga_2O_3$, including the compound $2Li_2O,Ga_2O_3,3B_2O_3$, was investigated by infra-red absorption spectra.[1097] The ultra-violet absorption spectrum of pentavalent vanadium in alkali-borate glasses has been studied.[641A]

Absorption and emission spectra of $Na_2O–B_2O_3$ glasses activated with europium[208], thulium[682A] and erbium[682A] have been studied. The spectra of alkali-borate glasses containing Co^{2+}, Ni^{2+} and Cu^{2+} are highly dependent on the composition of the base glass.[373] The absorption spectrum of $Fe^{2+}–Fe^{3+}$ in borax glasses has been studied.[39] Two forms of iron may be present under oxidizing conditions and three forms of iron under reducing conditions.[40] Studies have been made of the optical absorption of Mn^{3+} in binary alkali-borate glasses[638A], of copper ions in $Na_2O–B_2O_3–NaCl$ glasses[1057], and of cobalt in alkali borate–halide glass.[496] Induced optical and ESR spectra were studied in borate glasses containing titanium.[1192A, 1194A] Gadolinium in molten borax glass gives no fluorescence in the visible. The red fluorescence of gadolinium in borax beads when excited by an iron arc is due to impurities of other rare earths.[935] The absorption and fluorescence of Nd^{3+} in alkali-borate glasses show an inflection at about 24 mole-% alkali oxide.[329] A study has been made of the fluorescence of Dy^{3+}, Eu^{3+}, Sm^{3+} and UO_2^{2+} in sodium borate glasses.[384A] Glasses of composition $Na_2O,17B_2O_3$ containing sodium halides and europium oxide luminesced with fluoride, chloride or bromide present, but not with iodide.[228A] A thermoluminescent lithium borate, $Li_2O,2B_2O_3$, containing 0·1% of manganese has improved sensitivity to radiation, and its emission spectrum has been studied.[821, 1153, 1164, 1165] Samarium and manganese have been studied as activators in lithium tetraborate.[497] Silver-activated lithium-borate glasses show radiophotoluminescence and have been investigated as dosimeters.[1159] The luminescence of borate glasses activated with terbium has been investigated.[270A] Borates have been evaluated as activators in sulphate and silicate phosphors.[434] Infra-red studies of $Li_2O–B_2O_3–P_2O_5$, $Na_2O–B_2O_3–P_2O_5$ and $K_2O–B_2O_3–P_2O_5$ glasses have been carried out.[916]

THERMOCHEMICAL DATA

Data on the heat capacity, entropy, free-energy function, heat content, heat of formation, free energy of formation, and log K_p have been compiled, calculated and tabulated[1085] for molten and/or glassy Li_2O,B_2O_3, $Li_2O,2B_2O_3$[780, 1085], $Li_2O,3B_2O_3$[1085], $Li_2O,4B_2O_3$[1085], Na_2O,B_2O_3[1085], $Na_2O,2B_2O_3$[780, 1085], $Na_2O,3B_2O_3$[783], $Na_2O,4B_2O_3$[780], $K_2O,2B_2O_3$[1085] and $K_2O,4B_2O_3$.[780, 1085]

The heat capacities of $Na_2O–B_2O_3$ glasses containing 7·87, 13·7 and 21·09 mole-% of Na_2O have been determined and tabulated from about 55 to 295°K.[856] Heat capacities of selected glasses in the five alkali-metal borate systems have been reported over a range of high temperatures.[1177] The specific heat of fused borax, 0·307 at 750°C, increased to 0·434 g cal deg^{-1} g^{-1} at 950°C.[303A]

Enthalpy changes of Na_2O–B_2O_3 glasses in the temperature interval between 50 and 298°K were calculated from low-temperature heat-capacity studies.[828] Heat contents of Li_2O–B_2O_3, Na_2O–B_2O_3 and K_2O–B_2O_3 glasses containing 0 to 33 mole-% metal oxide have been determined from 25° to 1100°C.[783]

The integral and relative partial enthalpies and entropies of mixing molten boric oxide and molten rubidium metaborate have been calculated.[3] The partial enthalpies of solution of boric oxide in Li_2O–B_2O_3 and K_2O–B_2O_3 have been measured and discussed in terms of immiscibility and structure.[918]

The heats of solution of Na_2O–B_3O_3 glasses are more exothermic when the glasses have been densified by applying high pressure.[798–9] This may be due to increased strain. At 20 mole-% Na_2O, a 50% change in the heat of solution was caused by high pressure.

From heats of solution of crystalline and glassy compositions in the systems Li_2O–B_2O_3, Na_2O–B_2O_3 and K_2O–B_2O_3, in nitric acid, heats of formation were calculated. The heats of solution of the glasses showed a minimum at 20 mole-% alkali oxide. In the crystallized systems, the minimum heat of solution occurred at compositions $Li_2O,3B_2O_3$, $Na_2O,4B_2O_3$ and $K_2O,4B_2O_3$.[750]

Mass-spectrometric experiments with an effusion cell[132] gave heats of sublimation, vaporization and dimerization as follows:

$LiBO_2(c) = LiBO_2(g)$, ΔH_s at 1060°K $= 79 \pm 3$ kcal
$LiBO_2(l) = LiBO_2(g)$, ΔH_v at 1160°K $= 70 \pm 3$ kcal
$2LiBO_2(g) = Li_2B_2O_4(g)$, ΔH at 1120°K $= -67 \pm 3$ kcal
$NaBO_2(c) = NaBO_2(g)$, ΔH_s at 1070°K $= 73 \pm 3$ kcal
$2NaBO_2(g) = Na_2B_2O_4(g)$, ΔH at 1070°K $= -53 \pm 3$ kcal

From the vapour pressure of molten lithium metaborate at 1120°–1280°C, the heat of sublimation was calculated to be $86{\cdot}3 \pm 3$ kcal mole of $LiBO_2$ and the heat of formation of $LiBO_2(g)$ was calculated to be $-157{\cdot}9$ kcal $mole^{-1}$ at 298°K.[327] The heat of formation has been compared with those of lithium fluoride and chloride.[128A] For the reaction $Li_2O(g) + B_2O_3(g) = 2LiBO_2(g)$, $\Delta H_{298} = -75$ kcal.[327]

For $Na_2O,2B_2O_3$ the heat of vaporization, from vapour pressure measurements, is 62·0 kcal $mole^{-1}$.[439] For $K_2O,2B_2O_3$ the heat of sublimation is 11·3 kcal $mole^{-1}$.[439]

The heats of fusion of $LiBO_2$ and $NaBO_2$ were determined from phase diagrams of the systems $LiBO_2$–LiF and $NaBO_2$–NaF as 7400 and 8000 g cal $mole^{-1}$, respectively.[649]

DTA curves have been determined for glasses of the composition $Na_2O,2B_2O_3$, $Na_2O,3B_2O_3$ and $Na_2O,4B_2O_3$.[135] The sodium oxide activity in Na_2O–B_2O_3 melts has been studied.[1235]

DISSOLVING OF ALKALI-BORATE GLASSES

The rate of dissolution of Na_2O–B_2O_3 glasses in hydrochloric acid has been found to vary in correspondence with maxima and minima in the liquidus curve of the phase diagram. The results were considered to indicate that the glass contained predominantly $B_3O_{4{\cdot}5}$ in the B_2O_3-rich region, and that the $B_8O_{13}^{2-}$ concentration increased as the composition $Na_2O,4B_2O_3$ was approached.[576]

The relative rates of dissolution of alkali-metal borate glasses of the composition $qM_2B_4O_7 + (1-q)B_4O_6$ in water at 100°, 75° and 50°C are about 25, 5 and 1, respectively, when $q = 1$, and about 5, 2 and 1 respectively when $q = 0$. The lowest rate of dissolution of Na_2O–B_2O_3 glasses is at $q = 0{\cdot}5$–$0{\cdot}7$ and that of K_2O–B_2O_3 glasses is at $q = 0{\cdot}4$–$0{\cdot}6$.[862] An attempt was made to find a general expression for the rate of dissolution.[590A] A study of the rate of dissolution of vitreous borax in water as a function of the stirring rate has indicated that the interface temperature gradient is about 3°C in unstirred water.[603] Studies of the rate of dissolution of Na_2O–B_2O_3 glasses in water at 5°–29°C showed that the lowest rate of solution occurred with glasses containing 25 mole-% Na_2O, and that the calculated activation energy reached a maximum at about 15 mole-% Na_2O.[194]

The effect of tempering Na_2O–B_2O_3 glass on its rate of dissolution in water and other properties has been discussed.[254] In experiments with discs of Na_2O–B_2O_3 glasses rotating about a diameter in water at 70°C, increased speed of rotation gave an increased rate of solution when the glass contained less than 5 mole-% of Na_2O, and a decreased rate of solution with 8–30 mole-% Na_2O.[255] Tempered glasses generally dissolved more rapidly than annealed glasses.[255] The rate of dissolution of borax glass in citric acid, glycine, hydrochloric acid and acetic acid has been measured, and activation energy values calculated.[600] The water 'solubility' of glasses in the systems Li_2O–B_2O_3–P_2O_5, Na_2O–B_2O_3–P_2O_5 and K_2O–B_2O_3–P_2O_5 has been determined.[916]

VOLATILIZATION AND VAPOUR PRESSURE

The alkali-metal metaborates volatilize congruently. The vapour pressure of lithium metaborate in the range 1120–1280°C, determined by the torsion–effusion method, can be represented by the equation $\log P_{\text{atm}} = -16{,}450/T + 8{\cdot}586$.[327, 1131] The volatilization of alkali-metal metaborates has been studied by mass spectrometry.[132, 1244] The vapour pressure of lithium metaborate, estimated by this means to be 2×10^{-6} atm at 1160°K[132], agrees well with that determined by the above torsion–effusion method.[327] The vapour pressure of the dimer $Li_2B_2O_4$ at 1160°K was similarly estimated to be 2×10^{-7} atm.[132]

In experiments at 1200°C, the rate of volatilization of molten Na_2O–B_2O_3 and K_2O–B_2O_3 was relatively low at high and low concentrations of alkali-metal oxide. The most rapid volatilization occurred at compositions between 0·8 and 1·6 moles of Na_2O (or 1·6 to 2·6 moles of K_2O) per mole of B_2O_3. If the original composition contained less than about 0·83 moles of Na_2O (or 0·67 moles of K_2O) per mole of B_2O_3, the vapour was considerably more alkaline than the original composition. Melts more alkaline than metaborate gave vapours usually somewhat less alkaline than the original composition, but not greatly different from it.[820]

At 800°C, the loss from fused borax due to volatilization is negligible if it is heated in a covered crucible for less than two hours.[427] However, under other conditions there is appreciable loss by volatilization.[124–5] Molten borax at 1150°–1300°C volatilized with an average vapour composition Na_2O 51·6%, B_2O_3 48·4%.[175] At 1200°C the vapour contained 42·4 to 43% of Na_2O[581, 820]; at 1400°C the vapour phase contained 30% of Na_2O,B_2O_3.[785]

Vapour pressures of molten sodium metaborate and disodium tetraborate assuming normal vapour densities have been measured by the transpiration method[175], and results are given in Table XXV; these results may not, however, be reliable, since the apparent vapour pressure increased with decreasing flow rate.[132]

Table XXV.—Vapour Pressures of Sodium Metaborate and Borax Melts[175]

Temperature, °C	Na_2O,B_2O_3, mm Hg	$Na_2O,2B_2O_3$, mm Hg
1150	2·55	2·1
1200	7·2	5·5
1250	28·0	13·0
1300	62·0	25·5
1350	160	
Calc. b.p.	1,434°C	1,575°C
Heat of vaporization	96,910 g cal	72,410 g cal

Estimates from mass-spectrometric data at 1070°K gave 5×10^{-7} atm for the vapour pressure of sodium metaborate and 2×10^{-8} atm for the dimer, $Na_2B_2O_4$.[132] Dipotassium tetraborate, $K_2B_4O_7$, has a higher vapour pressure than disodium tetraborate, $Na_2B_4O_7$, and its vapour pressure increases more with an increase in temperature. Vapour pressures have been measured by the effusion method[439], and results are given in Table XXVI.

Table XXVI.—Vapour Pressures of $Na_2O,2B_2O_3$ *and* $K_2O,2B_2O_3$ *Melts*

$Na_2O,2B_2O_3$		$K_2O,2B_2O_3$	
Temp., °C	Vapour pressure, Torr × 10^3	Temp., °C	Vapour pressure, Torr × 10^3
763	0·69	758	1·9
793	1·14	778	4·7
812	1·8	797	12·6
871	2·6	820	44
872	7·3		
940	45		

Studies of the volatility and the compositions of the vapour phase and condensate have shown that Na_2O,B_2O_3 is completely volatile at 1400°C without change in composition. The condensate from $2Na_2O,B_2O_3$ volatilized at 1400°C consists of Na_2O,B_2O_3 and that from $Na_2O,2B_2O_3$ contains 30% of Na_2O,B_2O_3.[785] In the K_2O–B_2O_3 system K_2O,B_2O_3 and $2K_2O,B_2O_3$ are completely volatile at 1300°C. $K_2O,2B_2O_3$ when vaporized gives a condensate consisting of K_2O,B_2O_3.[785] Li_2O,B_2O_3 and $Li_2O,2B_2O_3$ vaporize at 1400°C. Volatilized $2Li_2O,B_2O_3$ changes to Li_2O,B_2O_3 in the vapour.[785] In borosilicate glass manufacture, the most volatile constituent is K_2O,B_2O_3.[785]

The volatility and composition of the vapour phase in the Rb_2O–B_2O_3 system has been studied over a range of 33–67 mole-% Rb_2O at 1100–1400°C.[785] The vapour pressure was determined over a range of 4·2 to 50 mole-% Rb_2O at 878°–1353°C. The heat of vaporization was $47{\cdot}3 \pm 0{\cdot}8$ kcal in this temperature range. The vapour composition was close to $RbBO_2$ in this range of composition. The activity of rubidium metaborate, $RbBO_2$, was essentially zero in Rb_2O–B_2O_3 melts containing 0 to 16 mole-% of Rb_2O, but it increased rapidly at higher Rb_2O concentrations.[3, 1141]

Molten cæsium metaborate, $CsBO_2$, distils without decomposition at about 800°C.[477] A study of its vapour pressure between 1038 and 1361°K indicated that its heat of vaporization is $41{\cdot}3 \pm 4$ kcal mole^{-1} of $CsBO_2$.[91A]

STRUCTURE OF ALKALI-BORATE VAPOURS

Mass-spectrometric and effusion studies have indicated the presence of monomeric, dimeric and trimeric lithium and sodium metaborates in the vapour phase over lithium and sodium metaborate at 750°–920°C.[131] There was about 90% of the monomer, and an appreciable amount (*ca.* 10%) of the dimer, but only a small amount (0·1%) of the trimer.[132] Other mass-spectrometric studies of alkali metaborate vapours have indicated that ionization of the monomer increases sharply from lithium to cæsium metaborate.[701]

Infra-red spectra suggest the structure $M^+(O^-{-}B^+{-}O^-)$ for the gaseous alkali-metal metaborates.[128] Electron-diffraction studies have indicated that there is a weak bond between the lithium, sodium or rubidium atom and the BO_2 group[677], and that the $NaBO_2$ and $LiBO_2$ molecules are planar with the M–O–B angle 90–110°.[7, 8] The electron-diffraction patterns of lithium and sodium metaborate vapours practically coincide.[678] Mass-spectrographic studies have indicated the presence of M^+, MBO_2^+ and $M_2BO_2^+$ [9, 132], and B^+, BO^+ and BO_2^+.[9] An electron-diffraction study of the $LiBO_2$ molecule gave 1·258 Å for the B–O distance.[240] Alkali-metal borate vapours have been studied 'chemically'.[784A] Information on the gaseous alkali-metal metaborates has been summarized.[1123]

Infra-red spectra of $NaBO_2$, $LiBO_2$, KBO_2, $RbBO_2$ and $CsBO_2$ molecules isolated in a matrix of solid argon or krypton suggest a C_2 molecular symmetry and an M–O–B bond angle in the neighbourhood of 90°.[745]

The equilibrium constant for the reaction $NaCl(g) + HBO_2(g) = NaBO_2(g) + HCl(g)$ at 1980 K has been determined to be $K_p = 2{\cdot}50$.[1121] Mixtures of sodium metaborate and sodium fluoride form mixed dimers on volatilization, and the problem of interpreting the mass spectra of the vapour has been discussed.[426A]

Chemical Reactions and Phase Equilibria

REACTION WITH WATER AND DEVITRIFICATION

The solubility of water vapour in alkali-borate melts containing 0 to 40 mole-% of Li_2O, Na_2O or K_2O is proportional to the square root of the partial pressure of water vapour. At 1 atm of steam and 900°C, 0·5 to 2·2 mole-% of H_2O, depending on the alkali-oxide: B_2O_3 ratio, are dissolved at equilibrium.[262] The solubility is at a minimum at 25 mole-% K_2O or 35–40 mole-% Na_2O.[262] In a study at 1100–1200°C, minima in the solubility of water in $Na_2O–B_2O_3$ melts were observed at the Na_2O,B_2O_3 and $Na_2O,4B_2O_3$ compositions, and a maximum was observed at $Na_2O,3B_2O_3$. In the eutectic compositions, a minimum was observed at 73·5% B_2O_3 and a maximum at 68·5%.[240A]

Alkali-metal borate glasses, as usually obtained by dehydration of hydrated borates, retain an appreciable amount of water. For example borax glass, as prepared in the laboratory by fusion in a current of dry air, lost a further 0·2% in water content by heating to constant weight.[781] Crystalline anhydrous borax, when melted in air, increased slightly in weight owing to absorption of water.[581]

All the anhydrous borate glasses are more or less hygroscopic. The tendency for $Na_2O–B_2O_3$ glasses to pick up moisture from the atmosphere increases as the boric oxide content is increased from 77 to 87 wt-%.[976] Anhydrous borax produced by calcining or by spraying borax solution on hot granular anhydrous borax is more hygroscopic than that made by fusion.[971]

When borax is melted in the presence of steam, some of the boric acid content is volatilized. The molar ratio $B_2O_3:Na_2O$ in the residue changes from 2 to 1·4.[495]

System $Li_2O–B_2O_3$. The devitrification rate has been studied by differential thermal analysis[1245, 1099, 1100] and by *X*-ray diffraction[719A] in glasses crystallizing to form lithium metaborate and tetraborate. $Li_2O–B_2O_3$ glasses containing more than 80% of B_2O_3 were attacked by atmospheric moisture in less than one month.[724] Electron microscope studies of $Li_2O–B_2O_3$ glasses containing 0–20 mole-% Li_2O showed the beginning of devitrification before the sample became turbid. Possibly two liquid phases appear at less than 10 mole-% Li_2O in a narrow temperature range.[453]

System $Li_2O–BeO–B_2O_3$. The 'glass region', devitrification and resistance to steam have been studied.[553, 556]

System $Li_2O–B_2O_3–MgO$. Devitrification and resistance of these glasses to moist air have been studied.[552, 556] Increased magnesium oxide concentration gives increased resistance to boiling water.[543]

System $Li_2O–B_2O_3–Al_2O_3$. Devitrification and other properties of this system have been studied.[140]

System $Li_2O–B_2O_3–SiO_2$. In this system glasses high in silica have low melting points and high durability.[722]

System $LiBO_2–Li_2MoO_4–MoO_3–BeO$. Nucleation was increased by the addition of lithium metaborate in the crystallization of beryllium oxide from its solution in molten $Li_2MoO_4–MoO_3$.[37]

System $Na_2O,4B_2O_3–Li_2O,SiO_2–SiO_2$. Devitrification has been studied as a function of temperature and sodium oxide content.[873]

System $Na_2O–B_2O_3$. The crystallization behaviour of borax glass has been studied.[198] Reference differential thermal curves of quenched $Na_2O,2B_2O_3$, $Na_2O,3B_2O_3$ and $Na_2O,4B_2O_3$ glasses have been published, showing devitrification and melting.[135]

Systems $Na_2B_4O_7–B_2O_3$, $Na_2B_4O_7–MgO$, $Na_2B_4O_7–3CaO,P_2O_5$, $Na_2B_4O_7–Al_2O_3$, $Na_2B_4O_7–ZnO$, $Na_2B_4O_7–PbO$. The crystallization characteristics of these and other more complex systems were studied in a temperature–gradient furnace.[653]

System Na_2O–BeO–B_2O_3. The devitrification products in this system have been studied. The resistance to moist air is less than that of Li_2O–BeO–B_2O_3 glasses.[554, 556]

System Na_2O–MgO–B_2O_3. Devitrification and resistance of these glasses to moist air have been studied.[552, 556]

System Na_2O–B_2O_3–SiO_2–ZrO_2. Crystals which form from the glasses of this system have been identified.[870]

Systems Na_2O–B_2O_3–SiO_2 *and* K_2O–B_2O_3–SiO_2. Glasses in these systems have properties which make them suitable as glaze components.[895A]

System K_2O–BeO–B_2O_3. These glasses are more hygroscopic than Na_2O–BeO–B_2O_3 or Li_2O–BeO–B_2O_3 glasses. The glass region has been determined.[555–6]

System K_2O–MgO–B_2O_3. Devitrification and resistance to moist air have been studied.[552, 556]

Borates in Glasses and Glazes

Borax, when added to container glass batches, was found to increase the rate of melting and refining, and in limited amounts it decreased the viscosity and thermal expansion and raised the annealing temperature.[12, 212A, 1230, 739A] It also has advantages in glazes.[775A, 1103] The effect of borates on the properties of soda–dolomitic–lime–silica glass[1250] and their effect on crystallization of a soda–potash–lime–silica glass have been investigated.[890A] The role of borates in glass technology has been discussed in a series of papers.[905–9]

REACTIONS WITH METALS AND CARBON

Tungsten is corroded by molten Na_2O–B_2O_3, the rate being controlled by diffusion of oxygen to the metal surface or by diffusion of the reaction product into the melt.[644A]

Molten $Na_2O,2B_2O_3$ and Na_2O,B_2O_3 at 1100°C corrode steel plates along grain boundaries, but the corrosion is less than with the corresponding sodium silicates.[65]

The corrosion rate of iron in molten mixtures of borax and the fluorides of lithium, sodium or potassium increases slowly with fluoride content but rapidly with ferric oxide content.[423] Corrosion of iron in molten chlorides in the presence of anhydrous borax has been studied.[422A] When steel was treated with 0·4–1 kg of borax per ton, it took up 0·0005–0·0015% of boron, improving its properties.[157]

Powdered mixtures of anhydrous borax and aluminium at 1300°C produced sapphire whiskers up to 20 mm long within a few minutes.[14]

Molten borax is appreciably reduced by carbon, the reaction beginning at 900°C; active carbon gives a more rapid reduction than graphite or coke.[400] Molten borax has been said to react with carbon in an oxygen-free atmosphere at 1000°–1200°C to form metallic sodium.[1029] Borates, when dissolved or suspended in molten salts, react with various chlorinating and reducing agents to give boron trichloride.[1195A]

REACTIONS WITH SALTS AND OXIDES

Borax fused with sodium carbonate forms $2Na_2O,B_2O_3$ or $3Na_2O,B_2O_3$ with loss of carbon dioxide, but the reaction is not complete.[958] When the fusion product is dissolved and borax added, sodium metaborate is formed in the solution.[958] From the carbonate content of various Na_2O–B_2O_3 melts in equilibrium with 1 atm of carbon dioxide, the variation of oxygen-ion activity with composition and temperature has been calculated.[644] From the weight loss of B_2O_3–M_2CO_3 mixtures (where $M = Li$, Na or K), with and without added sodium sulphate, when heated at 1000°C in a stream of carbon dioxide, the equilibrium constants for the reaction $Na_2O,B_2O_3 + Na_2CO_3 = 2Na_2O,B_2O_3 + CO_2(g)$ have been calculated.[252] These equilibrium constants decreased in the order Li, Na, K.[252] In the reaction of boric oxide with carbonate in a fused mixture of sodium and potassium chlorides at 750°C, there were inflections in the oxygen electrode potential at certain $B_2O_3:CO_2$ ratios, suggesting the formation of compounds in the melt.[1232]

At 150°C anhydrous borax gradually reacted with an $AlCl_3$–NaCl melt. After three days, analysis of liquid and solid phases indicated that 59% of the boron was in the melt, 7% was undissolved, and 34% had volatilized, probably as boron trichloride or boron oxychloride.[1126]

When boric oxide or borax was dissolved in fused $NaAlCl_4$, and hydrogen was bubbled through the melt at 500°–700°C, the presence of diborane was detected in the products condensed at −196°C.[1021]

Borax, mixed with 0·25 to 1 part by weight of ammonium chloride and heated in a stream of ammonia at 850°–2000°C for 2 h, produces boron nitride.[1020]

Molten alkali borates are good solvents for minerals[263] and metal oxides, some of which dissolve with the evolution of heat.[202] The solubility generally increases with alkali-metal content and with temperature. When the molten solutions are cooled, in some cases crystals of the metal oxide are formed; in other cases compounds are formed. A compilation of relevant phase-equilibrium diagrams, which includes many systems containing borates, has been published, with a supplement in 1969.[1109]

Many substances have been crystallized by dissolving them in molten sodium metaborate, and evaporating the solvent (ref. 1083, No. 21, p. 653). Studies of cryoscopy in lithium metaborate are included in a review published in 1961.[1080] The molar freezing-point lowering for titanium dioxide and nickel oxide[193] and for beryllium and magnesium oxides[936] in lithium metaborate approaches the normal value for one particle as the concentration approaches zero. In solutions of the oxides Al_2O_3, Fe_2O_3, Co_2O_3 and Cr_2O_3 in fused lithium metaborate there is evidence for ionization of the type $AlO_2^- + AlO^+$.[936] The freezing-point lowering of the halides LiF, NaF, KF, BeF_2, ZnF_2, CdF_2, PbF_2, AlF_3 and Na_3AlF_6[937], and LiCl, NaCl and $BaCl_2$[193] in molten lithium metaborate indicated that all these compounds were completely ionized. Freezing-point studies of lithium, sodium and barium chlorides in fused lithium metaborate indicated that the molar lowering is 15.[938] A description of the experimental method has been published.[692] Lithium metaborate has been studied as a solvent for dissolving and crystallizing zirconium dioxide.[521] $LiGa_5O_8$ has been grown from a solution of gallium oxide in lithium borates.[529] Crystals of $LiFeO_2$, $LiFe_5O_8$ and Fe_2O_3 may be grown from solutions of ferric oxide in molten lithium borates.[15] Lithium metaborate, when heated with an equimolar amount of cobaltous oxide at 770°C, under nitrogen largely free of oxygen, forms $LiCoBO_3$. The same compound can be made by melting a mixture of one mole of Co_3O_4 with nine moles of $LiBO_2$ and extracting the unreacted metaborate with boiling methanol.[481]

Molten disodium tetraborate, $Na_2B_4O_7$, used as a mineralizing additive, increased the rate of formation of sodium aluminate at temperatures above 900°C.[159A]

The solubility of silver oxide in molten Na_2O–B_2O_3 has been determined at 825°–935°C as a function of sodium oxide content and oxygen partial-pressure.[518] Silver oxide acts as a network modifier like the alkali oxides. The diffusion coefficient of Ag^+ in a 15% Na_2O–85% B_2O_3 melt has been measured.[620]

The solubility of beryllium oxide in molten Na_2O–B_2O_3 increases slowly as the sodium oxide content is increased to about 0·15 mole per mole of boric oxide. It then increases more rapidly as the sodium oxide is increased to 0·4 mole.[89A] On cooling, beryllium oxide crystallizes.[256]

The solubility of alumina in Na_2O–B_2O_3 melts increases with alkali content.[256] β-Alumina crystals will grow from molten borax; addition of lead oxide will give corundum.[53] Whiskers containing three aluminium borates have been made by dissolving aluminium oxide in fused borax at 1400°C and cooling to 1000°C.[367] The relation between $9Al_2O_3,2B_2O_3$ and $2Al_2O_3,B_2O_3$ has been studied in the system Na_2O–B_2O_3–Al_2O_3.[1147A] In small-scale experiments, no crystallization occurred in this system.[135] Alumina ceramics for metal cutting are stronger if polished in molten borax.[405] Equations for the rate of dissolving of solids in melts were developed and found to apply to the dissolving of corundum in molten $Li_2B_4O_7$.[333]

Yttrium iron garnet, $Y_3Fe_5O_{12}$ can be grown from its solutions in BaO–B_2O_3,

$Na_2O–B_2O_3$ or $K_2O–B_2O_3$.[529] Yttrium oxide, Y_2O_3, forms a yttrium borate with molten borax.[135] Molten sodium borates react with all rare-earth oxides except that of cerium at 900°C to give rare-earth orthoborates, RBO_3.[823] At low sodium contents, the metaborates, $R(BO_2)_3$, of praseodymium, samarium, gadolinium, terbium, dysprosium, erbium, ytterbium and lutetium are formed.[228] The orthoborates of dysprosium, holmium, erbium, thulium, ytterbium and lutetium are obtained at $B_2O_3:Na_2O$ ratios from 2:1 to 17:1, but those of praseodymium, samarium, europium, gadolinium and terbium are obtained only at $B_2O_3:Na_2O$ ratios from 2:1 to 7:1.[823] Compositions of liquid phases in equilibrium at 900°C with $PrBO_3$, $Pr(BO_2)_3$, $SmBO_3$, $Sm(BO_2)_3$, $GdBO_3$, $Gd(BO_2)_3$, $TbBO_3$, $Tb(BO_2)_3$, $DyBO_3$, $ErBO_3$, $YbBO_3$ and $LuBO_3$ have been determined.[228] Lanthanum oxide, La_2O_3, forms lanthanum orthoborate, $LaBO_3$, with molten borax.[135, 823] At 900°C neodymium oxide added to molten $Na_2O–B_2O_3$ at 900°C, forms neodymium orthoborate, $NdBO_3$, if the $B_2O_3:Na_2O$ molar ratio is 2 to 3·72, but forms the metaborate $Nd(BO_2)_3$ if the $B_2O_3:Na_2O$ molar ratio is between 3·72 and 17.[822] Cerium dioxide apparently forms no chemical compounds when added to molten $Na_2O–B_2O_3$.[822]

The rate of dissolution of silica plates in molten borax at 900°–1200°C was found to be proportional to the time, after the time required to form the diffusion layer. These experiments indicated that diffusion through the boundary layer controlled the dissolution rate.[331, 333] Fused silica dissolves considerably more rapidly than quartz in molten borax at 845°C, but only a little more rapidly at 920°C.[332]

In $Na_2B_4O_7–TiO_2$ solutions containing 15–20% or more excess sodium oxide, and in $K_2B_4O_7–TiO_2$ solutions, titanates are formed on cooling.[610] $K_2Ti_6O_{13}$ crystals are formed by cooling a 25% solution of titanium dioxide in $K_2B_4O_7$.[610] From $Na_2B_4O_7–TiO_2$ and $Li_2B_4O_7–TiO_2$ solutions, however, titanium dioxide crystallizes as well-formed rutile crystals.[610] Single crystals of a variety of substances have been grown from molten borax.[617] These include Ti_3O_5, Ti_4O_7, Ti_5O_9, Ti_6O_{11}, Ti_7O_{13}, Ti_8O_{15}, $Ti_{10}O_{19}$ and rutile[56A], depending upon the oxygen pressure. Rutile of controlled composition has been grown from molten $Na_2O,3B_2O_2$ and $K_2O,3B_2O_3$.[79] The morphology of rutile grown from fused borax has been studied.[714A]

The solubility of titanium dioxide in $Na_2O–B_2O_3$ melts increases with alkali content, slowly at first, then very rapidly between 0·3 and 0·4 moles of Na_2O per mole of B_2O_3. Titanium dioxide is formed by cooling. The solubility of the oxides TiO_2, ZrO_2, SnO_2 and ThO_2 also increases with alkali content, and decreases with the molecular weight.[256]

The solubility of titanium dioxide in molten borax was determined to be: at 900°C 9·5; at 1000°C 11·5; at 1100°C 15·5; and at 1200°C 18·5 wt-%. Attempts to determine the solubility by quenching failed because of rapid crystallization.[368] Whiskers of titanium dioxide (rutile) were grown from fused borax by cooling from 900–1200°C.[368] Another solubility study[610] gave the solubility of titanium dioxide in molten borax (g per 100 g of $Na_2B_4O_7$) as follows:

Temperature, °C	730	815	860	886	920	972
Solubility, g 100 g^{-1} of $Na_2B_4O_7$	11	13	15	17	20	25·5

The solubility of titanium dioxide in the various molten borates, in g per 100 g of solvent, has been determined as follows (solid phase, rutile): $Li_2B_4O_7$, 12 at 940°C; $Na_2B_4O_7$, 23 at 940°C; $K_2B_4O_7$, 30 at 940°C; KB_5O_8, *ca.* 0·01 at 900°C; $Na_2B_4O_7$ + 8·2% NaOH, 30 at 900°C; $Na_2B_4O_7$ + 10% NaF, 25 at 893°C; $Na_2B_4O_7$ + 10·2% LiF, 30 at 952°C; $Na_2B_4O_7$ + 8% LiF, 20 at 880°C; $Na_2B_4O_7$ + 3% SnO, 17 at 880°C; B_2O_3, insoluble.[29] Solubility curves of titanium dioxide in lithium, sodium and potassium tetraborates have been determined.[29] The solubility of titanium dioxide and of molybdenum and tungsten trioxides in molten borax has been investigated at 800°, 900° and 1000°C.[760] The primary phase, at 20–50% metal oxide, is the metal oxide.[135] Crystalline fibres of titanium dioxide, zirconium dioxide and zircon can be made by crystallization from molten borax–boric oxide mixtures.[1027]

The solubilities of the oxides PbO, Bi_2O_3, NiO, ZrO_2, CuO, WO_3, Fe_2O_3, CdO, TiO_2 and MoO_3 in molten borax, at 760° and 800°C, respectively, have been determined.[203A]

The solubility of zirconium dioxide in molten borax has been reported as 1·68 wt-% at 900°, 4·60 at 1000°, and 7·38 at 1100°C.[368] Mixtures of borax and lithium chloride were suitable for growing zirconium dioxide (baddeleyite) whiskers by cooling from 1100°–1500°C.[368]

The solubility of lead oxide, PbO, in $Na_2B_4O_7$ is 37·5 mole-%, and in $K_2B_4O_7$ is 35 mole-%, at 850°C.[326]

Zirconium and thorium dioxides dissolve in molten borax and crystallize as the dioxides.[135] At least one part of germanium dioxide will dissolve in two parts by weight of molten borax.[251] The approximate structure of lithium borogermanate, Li_2O,B_2O_3,GeO_2 has been determined.[356A]

Vanadium pentoxide is not reduced when melted with borax. The solubility is about 1% of V_2O_5 at 800°, 6% at 920° and 12% at 1100°C.[747]

Niobium oxide, Nb_2O_5, dissolves in molten borax; the primary phase at low niobium oxide concentrations is sodium niobate, $NaNbO_3$[130,135,1135] and at higher concentrations it is $Na_2Nb_8O_{21}$ or a higher niobate. A phase diagram has been published for the ternary system $Na_2O–Nb_2O_5–B_2O_3$[135,1135]; it includes a large area of immiscibility.

Tantalum oxide, Ta_2O_5, when dissolved in molten borax, forms crystals of sodium tantalates.[135]

The solubility of bismuth oxide, Bi_2O_3, is 20·5 mole-% in $Na_2B_4O_7$ and 11·4 mole-% in $K_2B_4O_7$ at 850°C.[326]

The solubility of chromic oxide in $Na_2O–B_2O_3$ melts increases with the alkali content.[256] No compounds are formed between chromates and molten borates.[872] Single crystals of chromic oxide have been grown from its solution in $K_2B_4O_7$ or in a mixture of $K_2B_4O_7$ and lead oxide.[53] Uvarovite, $Ca_3Cr_2(SiO_4)_3$, a naturally occurring garnet, has been crystallized from a solution of its components in molten Na_2O,K_2O,1·3B_2O_3.[513A]

The solubility of tungsten trioxide, WO_3, in molten $Na_2O–B_2O_3$ increases with sodium oxide content and temperature. Tungsten trioxide crystallizes from melts high in boric oxide; sodium tungstate crystallizes when 0·2 to 0·3 mole of Na_2O is present per mole of B_2O_3.[256]

Molten borax dissolves ferric oxide; when the melt is cooled, ferric oxide flakes having a metallic lustre are formed. These can be recovered for use as a pigment by dissolving the borax in nitric acid.[89A, 999] When a mixture of borax and ferric oxide at 1000°C is reduced with hydrogen or carbon monoxide, ferrous boroferrite (Fe_2O_3,B_2O_3,4FeO) is formed and can be recovered by treatment with nitric acid.[158] The same product is obtained by heating a borax–iron mixture in nitrogen and oxidizing with air.[158] Single crystals of magnetite have been grown from a ferric oxide and borax mixture under 2 atm of argon containing 1 p.p.m. of oxygen, cooled at about 2°C h^{-1} from 1300° to 1000°C.[877]

An equimolar mixture of sodium orthoborate (Na_3BO_3), and ferric oxide, heated for 18 h at 1200°C in air, and leached with boiling water and hydrochloric acid, gave a mixture of green $FeBO_3$ crystals and black Fe_3BO_6 crystal plates.[920] From certain compositions in the molten system $Li_2O–B_2O_3–Fe_2O_3$ at 1100°C, single crystals of $LiFeO_2$, $LiFe_5O_8$ and α-Fe_2O_3 can be grown.[15] The approximate phase stability boundaries in this system have been determined.[15] Boroferrites of the formula Fe_2O_3,B_2O_3,4NiO, Fe_2O_3,B_2O_3,4CoO and Fe_2O_3,B_2O_3,4CuO have been prepared by dissolving the metal oxides in molten alkali borates and cooling slowly.[84] Ferric oxide has a higher solubility in molten alkali borates than chromic oxide; cobaltous oxide has a greater solubility than ferric or nickel oxide.[89A]

The solubility of nickel oxide in $Na_2O–B_2O_3$ melts increases slowly with sodium oxide content at first, and increases more rapidly when the molar ratio $Na_2O:B_2O_3$ is greater than about 0·25, to a maximum at a molar ratio of about 0·4–0·5.[89A] The solubility of nickel oxide in fused borax at 800°C is 10·4 mole-%.[611] On cooling, melts high in boric acid give an emulsion, and with increasing alkali content $2NiO,B_2O_3$, $3NiO,B_2O_3$ and nickel oxide are successively formed.[89A, 256] Nickel oxide is formed at $Na_2O:B_2O_3$ molar ratios above 0·35–0·4. The thermodynamic properties of nickel oxide dissolved in fused borax have been investigated by means of e.m.f. measurements.[611]

LIQUID–SOLID PHASE EQUILIBRIA

System $Li_2O–B_2O_3$, see p. 348.

System $LiBO_2–LiF$. A compound $2LiF,3LiBO_2$, and two eutectics at 67% $LiBO_2$ m.p. 688°C, and 80% $LiBO_2$ m.p. 710°C, exist.[412] Another study reported one eutectic at 59% $LiBO_2$, m.p. 725°C.[649]

System $LiBO_2–LiCl$. A eutectic exists at 15 mole-% $LiBO_2$, m.p. 584°C[494, 494A] or at 19 mole-% $LiBO_2$, m.p. 572°C.[659]

System $LiBO_2–NaCl$. This stable diagonal has a eutectic at 45 mole-% NaCl, m.p. 740°C.[494A] There is some tendency to form two liquids.[155]

Systems $LiBO_2$–NaCl, KCl, CsCl; $NaBO_2$–LiCl, CsCl; KBO_2–LiCl, NaCl, CsCl, LiF, LiBr. In these systems immiscibility occurs if the cations are sufficiently different.[155] Li–Na systems have a tendency to form two liquids, Li–K systems form two liquids and the Li–Cs system has a larger two-liquid region.

System $LiBO_2–LiCl–Li_2SO_4$. This system has a eutectic at 472°C.[659]

Systems $LiBO_2$—*Alkali-metal sulphates*, *chromates*, *molybdates*, *vanadates*, *nitrates*, *and carbonates*. Solubility in these reciprocal systems has been studied in terms of the polarizabilities of the ions.[156]

System $LiBO_2–LiPO_3$. This system is actually ternary. Congruently melting phases, m.p. 740°C (unidentified) and 1038°C (lithium orthophosphate), and an incongruently melting phase, m.p. 730°C (lithium pyrophosphate) exist. There are points of common crystallization of phases at 628°, 644° or 647°, and 810° or 812°C.[1216, 1214]

System $LiBO_2–Li_3PO_4$. A eutectic exists at 3 mole-% Li_3PO_4, 834°C[1213], or at 96 mole-% $(LiBO_2)_3$, 827°C.[1217]

System $Li_2B_4O_7–Li_3PO_4$. A glass was not formed in compositions containing more than 20 mole-% Li_3PO_4. There is a eutectic at about 2·5% Li_3PO_4, m.p. 905°C.[837]

System $Li_2O–B_2O_3–P_2O_5$. The compounds $Li_2O,11B_2O_3,13P_2O_5$ and $2Li_2O,3B_2O_3,P_2O_5$ probably exist.[837]

System $Li^+||BO_2^-, PO_3^-, SO_4^{2-}$. A thermal-analysis study indicated the formation of three congruently melting compounds: $LiBO_2,7LiPO_3$, m.p. 750°; $4LiBO_2,LiPO_3$, m.p. 1042°C; and $3Li_2SO_4,2LiBO_2$, m.p. 751°C; one incongruently melting compound, $LiBO_2,LiPO_3$; and a two-liquid region. There are ternary eutectics melting at 504° and 526°C.[1207]

System $Li^+||SO_4^{2-}, P_2O_7^{4-}, B_4O_7^{2-}$. The ternary eutectic melts at 733°C. There is a field of phase separation.[1211]

System $Li_2B_4O_7–Li_2SO_4$. There is a eutectic at 3·5 equiv.-% $Li_2B_4O_7$, m.p. 840°C.[1211]

System $LiBO_2–Li_2SO_4$. A compound $3Li_2SO_4,2LiBO_2$[411, 1206] the composition of which is given apparently incorrectly in another paper[76] as $3Li_2SO_4,2Li_2(BO_2)_2$, m.p. 742°C, and two eutectics, 18 mole-% $Li_2B_2O_4$, m.p. 737°C and 31 mole-% $Li_2B_2O_4$, m.p. 737°C occur in this system.[76, 411] A later study gave 743° and 748°C for the melting points of these eutectics.[1206]

System $LiBO_2–Li_2WO_4$. A compound, $2LiBO_2,3Li_2WO_4$, incongruent m.p. 710°C, and a eutectic at 8 mole-% $Li_2B_2O_4$, m.p. 686°C, exist.[75, 411] Another reference[78] gives the compound as $2Li_2(BO_2)_2,3Li_2WO_4$, m.p. 742°C.

System $LiBO_2$–Li_2SO_4–Li_2WO_4. This system has a eutectic at 590°C.[659]

System Li_3BO_3–Li_2CO_3. A continuous series of solid solutions is formed with a minimum melting point at 52 mole-% Li_3BO_3, m.p. 700°C. The lithium carbonate structure expands with increasing lithium orthoborate content, up to 60 mole-% Li_3BO_3.[483]

System Li_2O–MgO–B_2O_3. Compositions in this system having a tendency to devitrify have been determined.[543]

System $LiBO_2$–MgB_2O_4. This system has a eutectic at 26·5 mole-% MgB_2O_4, m.p. 790°C.[717]

System $LiBO_2$–CaB_2O_4. There are two eutectics, m.p. 773° and 769°C; and a compound $4LiBO_2,CaB_2O_4$.[717]

System $LiBO_2$–Al_2O_3. There are two eutectics, m.p. at 750° and 730°C, and two compounds, $2Li_2O,Al_2O_3,2B_2O_3$, m.p. 785 ± 10°C and Li_2O,Al_2O_3,B_2O_3, m.p. 760 ± 10°C.[1095]

System Li_2O–B_2O_3–Al_2O_3. Compounds $2Li_2O,B_2O_3,Al_2O_3$, m.p. 870°C and $2Li_2O,2Al_2O_3,3B_2O_3$, incongruent m.p. 790°C, occur in this system.[403]

System Li_2O–B_2O_3–$(Al_2O_3 + SiO_2)$. A diagram of this system has been published.[1251]

System $LiBO_2$–Ga_2O_3. The compound $2Li_2O,Ga_2O_3,3B_2O_3$, *d* 2·78 g/cm³, is formed in this system.[1097–8]

System Li_2O–B_2O_3–Fe_2O_3. Phase equilibrium has been studied at 950–1200°C.[15, 736]

System $LiBO_2$–B_2O_3–NiO. An estimated diagram has been published.[82] NiO, $3NiO,B_2O_3$ or $2NiO,B_2O_3$ may be formed, depending on conditions. There is a two-liquid area. The lowest eutectic is 813°C.[82]

System $Li_2O,3B_2O_3$–$Na_2O,3B_2O_3$. There is *X*-ray evidence for an unidentified ternary compound.[783]

System $Li_2O,2B_2O_3$–$Na_2O,2B_2O_3$. There is *X*-ray evidence for an unidentified ternary compound.[783]

System $LiBO_2$–$NaBO_2$. Early work (Mellor, V, 68, 79) indicated limited miscibility of the crystals, with a eutectic at 48 wt-% $NaBO_2$, m.p. 650°C, or 42 mole-% $NaBO_2$, m.p. 648°C. More recently, a eutectic was reported at 43 mole-% $NaBO_2$, m.p. 652°[1214]; 41·7 mole-% $NaBO_2$, m.p. 648°[717]; 42 mole-%, m.p. 648°[494]; or 44 mole-%, m.p. 652°C.[1206]

System Li_2O–Na_2O–B_2O_3–SiO_2. Phase equilibrium has been studied.[535A, 815, 873]

System $Li^+, Na^+ \| BO_2^-, SO_4^{2-}$. This system has ternary eutectics melting at 578° and 620°C[1206], and a double salt $3Li_2SO_4,2LiBO_2$.[1206]

System $(LiBO_2)_2$–Na_2SO_4. This system consists of three curves, corresponding to α-$LiBO_2$, β-$LiBO_2$ and Na_2SO_4, intersecting at 12 equiv.-% Na_2SO_4, 793°C, and 59·5 equiv.-% Na_2SO_4, 663°C.[1206]

System $Li^+, Na^+ \| BO_2^-, PO_3^-$. This is an unstable section of the complex quaternary system. In a large region in this system, $LiPO_3$ is converted into Li_3PO_4.[1214]

System $Li^+, Na^+ \| BO_2^-, PO_4^{3-}$. The ternary eutectic melts at 642°C and has the composition 50 mole-% $(LiBO_2)_3$, 7 mole-% Li_3PO_4 and 43 mole-% $(NaBO_2)_3$. Binary eutectics are at 96 mole-% $(LiBO_2)_3$–4 mole-% Li_3PO_4, m.p. 827°C; 62 mole-% $(NaBO_2)_3$–38 mole-% Na_3PO_4, 912°C; and 57·5 mole-% $(NaBO_2)_3$–42·5 mole-% Li_3PO_4 (stable diagonal) 772°C.[102A]

System $Li^+, Na^+ \| P_2O_7^{4-}, BO_2^-$. Two double salts are formed, $Li_4P_2O_7,4LiBO_2$, m.p. 1082°C and $Na_4P_2O_7,4NaBO_2$, m.p. 986°C. There are six ternary eutectics melting between 638° and 834°C.[1210]

System $LiBO_2$–KBO_2. A eutectic exists at 45 mole-% KBO_2, m.p. 618°C[717], or at 44 mole-% KBO_2, m.p. 582°C[78], or at 47·5 mole-% KBO_2, m.p. 602°C[494], or at 43 mole-% KBO_2, m.p. 606°C.[1217]

System $LiBO_2$–KCl. This is a stable binary system with a large area of immiscibility and a eutectic at 97·5 mole-% KCl, m.p. 730°C.[155,494].

System $Li^+, K^+ \| BO_2^-, Cl^-$. In all the binary systems in this reciprocal system, eutectics are formed: 47·5 mole-% KBO_2–52·5 mole-% $LiBO_2$, m.p. 602°C; 15 mole-% $LiBO_2$–85 mole-% LiCl, m.p. 584°C; 27·5 mole-% KBO_2–72·5 mole-% KCl, m.p. 723°C. There is a large area of liquid immiscibility.[494]

System $Li^+, K^+ \| SO_4^{2-}, BO_2^-$. The phase diagram has six solid phases in equilibrium with the melt including KBO_2, $Li_2(BO_2)_2$,K_2SO_4, α-$LiBO_2$, β-$LiBO_2$, $3Li_2SO_4$,-$2LiBO_2$, and ternary eutectics melting at 525°, 570° and 726°C.[75] The $3Li_2SO_4,2LiBO_2$ compound was stated in a later paper to be $3Li_2SO_4,2Li_2B_2O_4$.[76]

System $Li_2B_2O_4$–K_2SO_4. There is a eutectic at 55 mole-% $Li_2B_2O_4$, m.p. 730°C.[76]

System $Li^+, K^+ \| BO_2^-, PO_4^{3-}$. There are ternary eutectics melting at 594° and 730°C.[1217]

System $Li^+, K^+ \| BO_2^-, WO_4^{2-}$. The compound $3Li_2WO_4,2Li_2(BO_2)_2$[78], m.p. 742°C, or $3Li_2WO_4,2LiBO_2$[75,411] and ternary eutectics melting at 558°, 564° and 575°C, were found in this system.[78]

System $Li^+, K \| BO_2^-, Cl^-, SO_4^{2-}, WO_4^{2-}$. Rules for the representation of a quinary system were applied to this reciprocal system.[658]

System $Li^+, Cs^+ \| BO_2^-, Cl^-$. In this reciprocal system[494], the binary system $LiBO_2$–$CsBO_2$ forms the compound $3LiBO_2,2CsBO_2$, m.p. 682°C, and has eutectics at 35 mole-% $CsBO_2$, m.p. 674°C and at 27·5 mole-% $LiBO_2$, m.p. 580°C. The other binary systems form simple eutectics. The diagonal $LiBO_2$–$CsCl$ is a binary system with a eutectic at 99 mole-% CsCl, m.p. 633°C, and liquid immiscibility at 820°C from 6 to 97·5 mole-% CsCl. This immiscibility area is larger than in the $Li^+, K^+ \| BO_2^-, Cl^-$ system.

System $Li^+, Cs^+ \| BO_2^-, PO_4^{3-}$. A double borate, $3LiBO_2,2CsBO_2$, m.p. 672°C, and a double phosphate are formed. The binary system Cs_3PO_4–$(CsBO_2)_3$ has a eutectic at 24 mole-% $(CsBO_2)_3$, m.p. 676°C. The $(LiBO_2)_3$–Li_3PO_4 system has a eutectic at 4 equiv.-% Li_3PO_4, m.p. 827°C. The Li_3PO_4–$(CsBO_2)_3$ system has a eutectic at 73 equiv.-% $(CsBO_2)_3$, m.p. 590°C. The $LiBO_2$–Cs_2BO_2 system has eutectics melting at 570° and 670°C, and the compound $2CsBO_2,3LiBO_2$, m.p. 672°C. The ternary system has eutectics melting at 550°, 585° and 658°C.[1219]

System Na_2O–B_2O_3, see p. 380.

System $Na_2B_4O_7$–$NaBO_2$. Compounds $2Na_2O,3B_2O_3$, $4Na_2O,5B_2O_3$ and $4Na_2O,7B_2O_3$, incongruent m.p. 792° and 863°C, and a eutectic at 737°C were reported[869,871,874–5], but the 4:5 and 4:7 compounds have not been observed in later works.[570]

System $NaBO_2$–$LiCl$. In addition to the components, sodium chloride and lithium metaborate crystallize in this system.[155,494A]

System $NaBO_2$–NaF. There is a eutectic at 831°C and 60% $NaBO_2$.[649] No solid solutions are formed. Cryoscopy indicated that the BO_2^- ion is not dissociated in sodium fluoride.[746]

System $Na_2B_4O_7$–$(NaF)_2$. No compounds were reported; a eutectic exists at 20 equiv.-% Na_2F_2, m.p. 680°C.[73] Cryoscopy indicated that $B_4O_7^{2-}$ gave four particles in sodium fluoride, probably $3BO_2^-$ and BO^+.[746]

System $NaBO_2$–$NaCl$. A eutectic exists at 750°C and 68·5 mole-% NaCl.[494A]

System $Na_2B_4O_7$–Na_2Cl_2. A eutectic exists at 86% $Na_2B_4O_7$, m.p. 710°C.[726] There is a wide two-liquid region extending from 0·1 to 57 mole-% $Na_2B_4O_7$, and a double salt $Na_2B_4O_7$,NaCl.[73A]

System $NaBO_2$–KCl. This is a stable system with a eutectic at 67·5% KCl, m.p. 670°C.[494A]

System $Na_2B_4O_7$–KCl. A eutectic exists at 72·5% $Na_2B_4O_7$ and 660°C.[726]

System $Na_2B_4O_7$–NaCl–KCl. A minimum m.p. exists at 86% $Na_2B_4O_7$, 5% NaCl and 9% KCl, m.p. 640°C.[726]

System $NaBO_2$–RbCl. This is a stable system with a eutectic at 80 mole-% RbCl, m.p. 655°C.[494A]

System $NaBO_2$–CsCl. A stable system with a eutectic at 89 mole-% CsCl, m.p. 596°C.[155, 494A]

System $NaBO_2$–CsBr. A stable system with two liquids between 30 and 70 mole-% $NaBO_2$ and a eutectic at 96·5 mole-% CsBr, m.p. 610°C.[494A]

System $NaBO_2$–KI. A stable system with separation into two liquids between 30 and 70 mole-% $NaBO_2$.[494A]

System $NaBO_2$–RbI. A stable system forming two liquids between 10 and 80 mole-% $NaBO_2$.[494A]

System $(NaBO_2)_2$–Na_2SO_4. A eutectic exists at 78 equiv.-% Na_2SO_4, m.p. 806°C.[213A, 1206]

System $NaBO_2$–Li_2SO_4. This unstable diagonal has a fusion curve with four branches corresponding to Li_2SO_4, $LiBO_2$, Na_2SO_4 and $NaBO_2$.[1206]

System $Na_2O,4B_2O_3$–Li_2O,SiO_2. Three crystalline phases were found.[535A]

System Sodium borate–lithium silicate–silicon dioxide. Liquidus surfaces and fields of primary crystallization have been determined.[885]

System $NaBO_2$–$NaPO_3$. In early work one compound, $NaBO_2$,$NaPO_3$, m.p. 800°C, was found in this system (Mellor, V, 79). Later work showed the crystallization of three congruent-melting phases, m.p. 790°, 820° ($Na_4P_2O_7$) and 852°C (Na_3PO_4), and an incongruent melting phase, m.p. 570°C, in addition to the components, with eutectics at 11 mole-% $NaPO_3$, m.p. 846°; 28·6 mole-%, 780°; 55 mole-%, 770°; and 87 mole-%, 530°C.[1214, 1218] In a study of the viscosity of this system, it was found that the composition containing 60% $NaBO_2$ at 650–700°C contains crystalline particles in suspension and exhibits thixotropic properties.[883]

System $NaBO_2$–Na_3PO_4. There is a eutectic at 13 mole-% Na_3PO_4, m.p. 910°C.[1213]

System $NaBO_2$–$Na_4P_2O_7$. A visual polythermal and thermal-analysis study indicated that there was a maximum melting point, 980°C or 972°C[1213, 213A], at about 80 mole-% $NaBO_2$. The phase concerned was identified as Na_3PO_4, indicating that the system is an unstable section in the ternary system Na_2O–B_2O_3–P_2O_5.[1213] Early work had been interpreted as indicating that $3NaBO_2$,$2Na_4P_2O_7$ was formed. There are two eutectics, at 48 mole-% $NaBO_2$, m.p. 850°, and at 94 mole-% $NaBO_2$, m.p. 890°C.[1213]

System $NaBO_2$–$Na_4P_2O_7$–NaCl. Cryoscopic measurements on $NaBO_2$ have been made in the eutectic NaCl–$Na_4B_2O_7$.[685]

System $Na^+ \| BO_2^-, P_2O_7^{4-}, SO_4^{2-}$. Two eutectics were found in this system, melting at 734° and 769°C.[213A]

System $Na_2B_4O_7$–$NaPO_3$. There are a congruently melting compound, $2Na_2B_4O_7$,-$3(NaPO_3)_2$, m.p. 772°C[1208], an incongruently melting phase decomposing at 704°C and two eutectics, at 9 equiv.-% $Na_2B_4O_7$, m.p. 540° and tentatively at 95 equiv.-% $Na_2B_4O_7$, m.p. 632°C.[1208]

System $Na_2B_4O_7$–$Na_4P_2O_7$. A compound $Na_2B_4O_7$,$Na_4P_2O_7$, congruent m.p. 794°C, and two eutectics, 31·5 equiv.-% $(Na_2B_4O_7)_2$, m.p. 786°, and 49 equiv.-% $(Na_2B_4O_7)_2$, m.p. 688°C exist.[434A] Other work[72A] gave a eutectic at 50 equiv.-% $Na_2B_4O_7$, m.p. 696°C.

System $Na^+ \parallel B_4O_7^{2-}, PO_3^-, P_2O_7^{4-}$. This system contains two ternary, congruently melting compounds $2NaPO_3$,$Na_2B_4O_7$,$Na_4P_2O_7$, m.p. 845°, and $Na_2B_4O_7$,$Na_4P_2O_7$,-$4NaPO_3$, m.p. 794°, and a eutectic melting at 782°C.[1205]

System $Na_2B_4O_7$–$Na_4P_2O_7$–NaF. This ternary system has eutectics melting at 578° and 690°C.[434A]

System $Na_2^+ \parallel BO_2^-, PO_3^-, SO_4^{2-}$. In this system there are four eutectics, at 517°, 667°, 745° and 796°C.[541A]

System $Na_2B_4O_7$–$Na_4P_2O_7$–Na_2SO_4. There are eutectics melting at 680°, 725° and 695°C.[72A]

System $NaBO_2$–Na_2CrO_4. There is a eutectic melting at 742°C at 15 mole-% $Na_2B_2O_4$.[74, 869, 875]

System $Na_2B_4O_7$–Na_2CrO_4. A eutectic melting at 715°C exists.[875]

System $Na_2B_4O_7$–$NaBO_2$–Na_2CrO_4. Compounds $2Na_2O$,$3B_2O_3$ and $4Na_2O$,-$5B_2O_3$ (or $4Na_2O$,$7B_2O_3$), immiscibility, and eutectics at 680°, 752°, 715°, 737°C have been reported.[869, 875]

System $NaBO_2$–K_2CrO_4. This system is stable and has a eutectic at 37·5 mole-% $(NaBO_2)_2$, m.p. 784°C.[74]

System $NaBO_2$–MgB_2O_4. There is a eutectic at 800°C and 38 mole-% MgB_2O_4.[718]

System $NaBO_2$–CaB_2O_4. A eutectic exists at 28·5 mole-% CaB_2O_4, m.p. 855°C. The incongruent compound $2NaBO_2$,CaB_2O_4 is formed.[718]

System Na_2O–CaO–B_2O_3. The compound $3Na_2O$,2CaO,$5B_2O_3$ melts at 880°C, absorbs moisture very slowly from the air, and dissolves slowly in water; its *X*-ray pattern has been published.[1047]

System Na_2O–CaO–B_2O_3–SiO_2. The liquidus temperature was lowered and the tendency to devitrify was reduced by the addition of 5% (or less) of boric oxide.[582]

System $NaCaBO_3$–Na_2CO_3. Solid solutions are formed from 0 to about 10 mole-% Na_2CO_3 and from 0 to about 10 mole-% $NaCaBO_3$.[483]

System $Na^+, Ca^{2+} \parallel B_4O_7^{2-}, SO_4^{2-}$. In this system the compounds CaB_4O_7,$CaSO_4$, $Na_2B_4O_7$,$2CaSO_4$, $Na_2B_4O_7$,$2CaB_4O_7$ (presumably) and $CaSO_4$,$2Na_2SO_4$ were found. There was liquid immiscibility in the binary systems $Na_2B_4O_7$–Na_2SO_4 and $Na_2B_4O_7$–$CaSO_4$.[945]

System $Na_2B_4O_7$–ZnO. Seven maxima have been reported in the phase diagram, corresponding to various compounds. There is a eutectic at 70 mole-% ZnO, m.p. 900°C. The volatility was studied as a function of temperature, zinc oxide concentration and added boric oxide. The best solvent for growing zinc oxide crystals (giving high zinc oxide solubility and low volatility) is a melt containing 20 mole-% of B_2O_3 and 80 mole-% of $Na_2B_4O_7$.[615] The crystallization behaviour in a temperature-gradient furnace was studied.[653]

System $NaBO_2$–Al_2O_3. This system is pseudobinary. Above 40 mole-% Al_2O_3, the compound Na_2O,Al_2O_3,B_2O_3, *d* 2·62 g cm^{-3}, m.p. 1010°C, is formed.[1096]

System $NaBO_2$–Ga_2O_3. This system is also pseudobinary. Two compounds, $2Na_2O$,Ga_2O_3,$2B_2O_3$, m.p. 775°, and Na_2O,Ga_2O_3,B_2O_3, m.p. 890°C, are formed, with eutectics melting at 710°, 740° and 790°C.[716A]

System $Na_2B_4O_7$–Fe_2O_3. The phase equilibrium has been determined and single crystals of ferric oxide have been grown from $Na_2B_4O_7$–Fe_2O_3 and from $Na_2B_4O_7$–ZnO–Fe_2O_3 melts.[53]

System Na_2O–B_2O_3–SiO_2. A phase equilibrium study showed that the compound $Na_2O,B_2O_3,2SiO_2$ exists.[583]

System $Na_2O,4B_2O_3$–SiO_2. No compound formation occurs in this system. There is a eutectic melting at 724°C and a region of immiscibility.[267, 690]

System $Na_2B_4O_7$–NiO. A eutectic exists at 3 mole-% NiO, m.p. 735°C.[80A, 81] The solutions deviates only slightly from ideality.

System $Na_2B_4O_7$–MoO_3. A eutectic exists at 30% MoO_3, m.p. 590°C.[298]

System $Na_2B_4O_7$–Nb_2O_5. Sodium niobates $NaNbO_3$[130, 135, 1135] and $Na_2Nb_8O_{21}$[135, 1135] are formed.

System Na_2O–B_2O_3–Nb_2O_5. Phase equilibria and crystallization in this system have been studied by thermal analysis, *X*-ray diffraction and high-temperature and electron microscopy. A two-liquid area and $NaNbO_3$, Na_3NbO_4 and $Na_2Nb_8O_{21}$ were formed.[135, 1135]

System $Na_2B_4O_7$–V_2O_5. A phase equilibrium diagram of the $Na_2B_4O_7$–V_2O_5 system[604], based on DTA and *X*-ray investigations, shows the presence of eutectics at 610° (12·5% $Na_2B_4O_7$) and 590°C (35% $Na_2B_4O_7$) and three compounds at 19, 51 and 78% $Na_2B_4O_7$. Other investigators, working on a small scale, did not obtain crystallization.[135]

System $NaBO_2$–KBO_2. This system forms a continuous series of solid solutions with minimum m.p. at 46 equiv.-% KBO_2 m.p. 838°C[74, 874] or 840°C.[1218] Early work (Mellor, V, 79) had given this temperature as 850°C. An abstract of another paper[875] gives this temperature as 668°C; this appears to be a misprint.

System $Na_2B_4O_7$–$K_2B_4O_7$. This system has a continuous series of solid solutions with minimum m.p. at 35 mole-% $K_2B_4O_7$, m.p. 668°[874], 666°C.[73, 1208] In one abstract[875], there appears to be a misprint in the melting point.

System $Na^+, K^+ \| BO_2^-, B_4O_7^{2-}$. Compounds $2Na_2O,3B_2O_3$, $4Na_2O,5B_2O_3$ and $2K_2O,3B_2O_3$, and a compound having the probable composition $NaBO_2,3KBO_2$ have been reported. Eutectics are at 668°, 670°, 704°, 737°, 778° and 838°C.[874]

System $Na^+, K^+ \| F^-, B_4O_7^{2-}$. This system has low-melting eutectics, m.p. 632°, 633° and 658°C.[73]

System $Na^+, K^+ \| B_4O_7^{2-}, Cl^-$. This system contains a two-liquid area extending from one side of the system to the other, covering 64% of the area.[73A]

System $Na^+, K^+ \| BO_2^-, PO_3^-$. This system contains three fields of solid solutions and two ternary eutectics melting at 480° and 482°C.[1218]

System $Na^+, K^+ \| PO_3^-, B_4O_7^{2-}$. Three eutectics, melting at 496°, 505° and 664°C, exist.[1208]

System $Na^+, K^+ \| BO_2^-, P_2O_7^{4-}$. There are two isomorphous, congruently melting compounds, $Na_4P_2O_7,4NaBO_2$, m.p. 970°, and $K_4P_2O_7,4KBO_2$, m.p. 918°C, and two eutectics, m.p. 766° and 736°C.[1209]

System $Na^+, K^+ \| BO_2^-, PO_4^-$. This system contains solid solutions of the borates and solid solutions of the phosphates. The lowest eutectic between them melts at about 820°C. The diagonal $(NaBO_2)_3$–K_3PO_4 has a eutectic at 30 equiv.-% K_3PO_4, m.p. 840°C.[1219]

System $Na^+, K^+ \| BO_2^-, CrO_4^{2-}$. There are ternary eutectics melting at 727° and 774°C.[74, 875]

System $Na^+, K^+ \| B_4O_7^{2-}, CrO_4^{2-}$. This system contains two regions of immiscibility[875] and two fields of crystallization of solid solutions of sodium and potassium chromates and tetraborates.[72]

System $Na^+, K^+ \| BO_2^-, B_4O_7^{2-}, CrO_4^{2-}$. Incongruently melting compounds $2Na_2O,3B_2O_3$, $4Na_2O,5B_2O_3$ and $2K_2O,3B_2O_3$, a eutectic melting at 690°C, and two immiscibility regions have been reported. This bath has been recommended as a high-temperature molten-salt bath.[871, 875]

System K_2O–B_2O_3, see p. 397.

System $K_2B_4O_7$–K_2F_2. The compound $KF,2K_2B_4O_7$ forms a eutectic with potassium fluoride at 44 mole-% $K_2B_4O_7$, m.p. 712°C.[73]

System KBO_2–KCl. A eutectic exists at 27·5 mole-% KBO_2, m.p. 723°[494] or 715°C.[660]

System $K_2B_4O_7$–K_2Cl_2. In this system there is a two-liquid region extending from 6 to 61·5% $K_2B_4O_7$, and a double salt, $2K_2B_4O_7$,KCl.[73A]

System KBO_2–KCl–K_2SO_4. A ternary eutectic exists at 30 mole-% KBO_2 and 56 mole-% KCl, m.p. 640°C.[246]

Systems KBO_2–NaCl *and* KBO_2–NaI. These systems are unstable diagonals in the phase diagrams.[494A]

System KBO_2–K_2SO_4. A eutectic at 32 mole-% K_2SO_4, m.p. 860°C, was reported.[246–7] In other work, the eutectic was found to be at 57·5 equiv.-% $K_2B_2O_4$, m.p. 848°C[78A, 411]; an incongruently melting compound was found, evidently $6KBO_2,K_2SO_4$.[76, 78A]

System $K_2B_4O_7$–K_2SO_4. There is a eutectic at 6 mole-% K_2SO_4, m.p. 783°C, and liquid immiscibility in the range 10–70% $K_2B_4O_7$.[1215]

System KBO_2–KPO_3. The compound KBO_2,KPO_3 was reported earlier (Mellor, V, 79). In a later investigation, an unidentified congruently melting phase, m.p. 712°C, tetrapotassium pyrophosphate, m.p. 880°C, and eutectics at 13 mole-% KBO_2, m.p. 684°, 31·5 mole-% KBO_2, m.p. 600° and 77·5 mole-% KBO_2, m.p. 760°C, were found.[1216, 1218] The system is therefore ternary.[1216] These eutectics were previously thought to correspond to the binary compounds $2KPO_3,3KBO_2$ and $4KPO_3,KBO_2$.[78A]

System K_2O–B_2O_3–P_2O_5. The following compounds have crystallization fields in this system: K_3PO_4, $K_4P_2O_7$, $K_5P_3O_{10}$, KPO_3, KBO_2, $K_2B_4O_7$, $K_2B_6O_{10}$, $K_2B_8O_{13}$, BPO_4, $5K_2O,4P_2O_5,B_2O_3$ (congruent m.p. 712°C), a hypothetical compound $3K_2O,4P_2O_5,3B_2O_3$, and a compound of unknown composition with an incongruent m.p.[1212]

System $K_2B_4O_7$–$(KPO_3)_2$. Two congruently melting phases, m.p. 684° and 735°C, one incongruently melting phase, m.p. 764°C, and three eutectics melting at 662°, 705° and approximately 586°C[1208] were reported. A later paper[1215] gave melting points 677° and 750°C for the compounds having temperature maxima and 698°, 713° and 610°C for the eutectics.

System KBO_2–$K_4P_2O_7$. K_3PO_4 is formed between 15 and 26 mole-% $K_4P_2O_7$, melting incongruently at 850°C in this system[1213], which is therefore an unstable section of the ternary system K_2O–B_2O_3–P_2O_5.

System KBO_2–K_3PO_4. A eutectic exists at 20 mole-% K_3PO_4, m.p. 880°C[1213], or at 66·5 mole-% $(KBO_2)_3$, m.p. 906°C.[1217]

System $K_2B_4O_7$–KPO_3–K_2SO_4. There are eutectics melting at 604°, 585° and 684°C.[1215]

System KBO_2–$K_4P_2O_7$–K_2SO_4. This system contains the crystallization field of K_3PO_4 as well as those of the components, and has ternary eutectics melting at 838° and 862°C.[1260]

System $(KBO_2)_2$–K_2WO_4. There is a eutectic at 40 mole-% $K_2B_2O_4$, m.p. 808°C.[78, 411]

System $K^+ \| SO_4^{2-}, PO_3^-, BO_2^-$. Two eutectics, m.p. 630° and 740°C, were reported.[247] A later study indicated two congruently melting compounds, apparently incorrectly thought to be $3KBO_2,2KPO_3$ and $KBO_2,4KPO_3$, an incongruently melting compound, $3(KBO_2)_2,K_2SO_4$, and three ternary eutectics, m.p. 532°, 603° and 723°C.[78A]

System KBO_2–K_2CrO_4. There is a eutectic at 37 mole-% $K_2B_2O_4$, m.p. 830°C.[74, 875]

System $K_2B_4O_7$–K_2CrO_4. In this system there is a eutectic melting at 756°C.[875]

System $K^+ \| CrO_4^{2-}, BO_2^-, B_4O_7^{2-}$. This system contains an incongruent compound, $2K_2O,3B_2O_3$, and two eutectics, melting at 748° and 794°C.[71]

System KBO_2–KCl–K_2WO_4. This system contains a double salt, KBO_2,K_2WO_4, which does not exist in equilibrium with the liquid in the KBO_2–K_2WO_4 system, and a ternary eutectic melting at 604°C.[660]

System KBO_2–MgB_2O_4. There is a eutectic at 36 mole-% MgB_2O_4, m.p. 746°C.[718]

System KBO_2–CaB_2O_4. A eutectic exists at 32·2 mole-% CaB_2O_4, m.p. 858°C.[718]

System $K_2B_4O_7$–NiO. There is a eutectic at 4 mole-% NiO, m.p. 788°C. The solution behaviour is nearly ideal.[80A, 81]

System $K_2B_4O_7$–Fe_2O_3. Phase equilibria have been determined and single crystals of ferric oxide have been grown in this system.[53]

System $K_2B_4O_7$–PbO–Cr_2O_3. Phase equilibria have been determined and single crystals of chromic oxide have been grown.[53]

System Rb_2O–B_2O_3, see p. 403.

Systems $RbBO_2$–$NaCl$ *and* $RbBO_2$–NaI. These diagonals of the ternary systems are unstable.[494A]

System $Rb_2B_4O_7$–NiO. There is a eutectic at 2 mole-% NiO, melting at 710°C. The solution behaviour is nearly ideal.[80A, 81]

System Cs_2O–B_2O_3, see p. 408.

Systems $CsBO_2$–$NaCl$ *and* $CsBO_2$–$NaBr$. These systems are unstable diagonals in the ternary systems.[494A]

System $Cs_2B_2O_4$–Cs_2SO_4. A phase was found with a temperature maximum at 674°C. Eutectics exist at 667°C and 12·5 equiv.-% Cs_2SO_4, and at 673°C and 25 equiv.-% Cs_2SO_4.[911]

System $CsBO_2$–$CsPO_3$. Two phases, giving temperature maxima at 671° and 760°C, were found. Eutectics are at 16 equiv.-% $CsBO_2$, m.p. 627°, at 30 equiv.-% $CsBO_2$, m.p. 639° and at 85% $CsBO_2$, m.p. 629°C.[911]

System $Cs^+ \| BO_2^-, SO_4^{2-}, PO_3^-$. This system has ternary eutectics melting at 604°, 608° and 618°C.[911]

LIQUID–LIQUID PHASE EQUILIBRIA

System Na_2O–B_2O_3–Na_2SO_4. Sulphur dioxide is absorbed from mixtures with air by melts of the composition $Na_2O,7B_2O_3$, with formation of sulphate in the melt. A second liquid phase, largely sodium sulphate, is formed when the gas mixture is passed through the melt for a sufficient length of time at 975°C.[779] At 1200°C the Na_2O–B_2O_3–Na_2SO_4 systems forms two liquids when the sodium sulphate content is more than about 2 mole-%, if the sodium oxide content of the borate phase is 10–25 mole-%. If the borate phase contains 30 mole-% of sodium oxide, the sodium sulphate concentration may reach 5 mole-% or more without separating.[778] If the sodium oxide content is low, the sodium sulphate content of the borate phase is low also. This has led to a commercial method of production of technical boric oxide[266A, 1046, 1048–9, 1052, 1054, 1054A, 1071, 1074–6] by fusion of a mixture of borax and sulphuric acid and separation of the two liquids.

Systems Na_2O–B_2O_3–NaCl[66, 221, 795, 1055, 1138, 1140], Na_2O–B_2O_3–NaBr[219, 795, 1055, 1138] *and* Na_2O–B_2O_3-NaI.[1138] Molten sodium chloride, bromide and iodide are only very slightly miscible with molten boric oxide, as the latter is non-ionic. When the $Na_2O:B_2O_3$ molar ratio is less than 1·4 very little borate dissolves in the halide phase. The heavier liquid is richer in halide; the lighter is richer in borate. When sodium metaborate is added, polyborate salts are formed which are more miscible. When sufficient sodium metaborate has been added at 800–980°C, one liquid is formed.[219, 221] In a study of the liquid-phase equilibria, surprising irregularities in the solubility curve of sodium chloride at 810°C, and of sodium bromide and iodide at 800°C, in the sodium polyborate layer, and in the solubility of sodium polyborates in the sodium chloride layer at 800°C, were reported.[219, 221, 1138, 1140] These fluctuations were attributed by the authors to formation of addition compounds or polyborate groups in the melt, but they appear instead to be due to experimental difficulties involved in working at temperatures close to the freezing point.[120] Sodium metaborate and sodium iodide are not completely miscible at 980°C.[1138]

System KBO_2–B_2O_3–KCl. The two-liquid region has been determined.[66]

System Na_2O–B_2O_3–KCl. Experiments in which ^{22}Na-labelled sodium borate was equilibrated with potassium chloride at 830°C showed that the K^+ concentration was higher than that of Cl^- in the borate phase, and that the Na^+ concentration was higher than that of BO_2^- in the halide phase.[1142]

In a system consisting of a molten alkali-metal borate layer in equilibrium with another fused-salt phase, the distribution coefficients of elements such as cæsium, rubidium, barium, strontium, neodymium, europium and silver, added in microquantities, differ from each other and also vary greatly with the alkali-metal oxide content of the borate layer. This behaviour has led to processes in which molten alkali-metal borates are used in high-temperature separations by means of liquid–liquid extraction.[713, 1031, 1031A, 1190, 1143] The distribution of small amounts of various metal ions between molten Na_2O–B_2O_3 and molten alkali halides and nitrates has been studied as a basis for such ion-exchange processes.[713, 1145, 1143] A glass of the composition $Na_2O,3B_2O_3$ which had previously been saturated with sodium chloride while in the molten state has been found to be a good solid ion-exchanger for barium, strontium and europium when in contact with molten sodium nitrate at 550°C. Distribution coefficients for these ions and for ^{137}Cs + ^{22}Na have been determined by radioassay.[712, 1139]

SUBMICROSCOPIC IMMISCIBILITY IN GLASSES

Submicroscopic liquid-phase separation, metastable or stable, into droplets of diameter 8–250 Å occurs in some Na_2O–B_2O_3 and other glasses.[233A, 267, 267A, 268, 310A, 362A, 453, 460A, 520A, 570A, 691, 723, 754, 755, 763A, 777, 793A, 815, 881, 890, 944, 1180, 1231] In the molten alkali-metal borate systems the separation into two liquids is metastable, occurring only at temperatures below the stable liquidus curves, and may be brought about by annealing the glass after it has been cooled.[754] Consolute temperatures and the approximate regions of immiscibility (mole-% alkali oxide) are as follows: Li_2O–B_2O_3 660°C, 2–18; Na_2O–B_2O_3 590°C, 7–24; K_2O–B_2O_3 590°C, 2–22; Rb_2O–B_2O_3 590°C, 2–16; Cs_2O–B_2O_3 570°C, 2–20.[754] No opalescence is visible, but the separation may be seen by electron microscopy.[754]

A study has been made of the effect of phase separation on the mechanical and viscous properties of borate glasses.[613A] Continuous measurements of electrical conductivities of various $Na_2O–B_2O_3$ melts have been made during cooling. The Arrhenius conductivity plot for each melt shows a distinct change in slope, which is attributed to subliquidus phase separation.[890] The consolute temperature is 615°C at 15 mole-% Na_2O. The phase separation may explain other anomalies[755], such as internal friction.[1198A] The size of the phase-separated areas is decreased by applying high pressure.[798–9] The region of metastable immiscibility for the system Na_2O,-$4B_2O_3–SiO_2$ has been determined.[691, 1117] With prolonged annealing the two liquids disappear and the system forms a stable liquid and silica crystals or a mixture of $Na_2O,4B_2O_3$ and silica crystals, depending on whether the temperature is above or below the eutectic temperature of 675°C.[1117]

The system $Na_2O–B_2O_3–SiO_2$[267A] contains three regions of metastable subliquidus immiscibility. A three-liquid region was reported below the immiscibility surface[310A], but a later study indicated two rather than three phases near the centre of the immiscibility gap.[1170] The pore radius in acid-leached borosilicate glass is 8–10 Å and the pore volume decreases with boric oxide content.[944] In lithium borosilicate glasses the particle size of the dispersed phase is larger than in sodium borosilicate glasses.[723]

OXIDATION-REDUCTION EQUILIBRIA OF DISSOLVED METAL IONS

The colours given by various metal ions when dissolved in molten borax has led to the use of the 'borax bead' in qualitative analysis.[44, 138, 876A] A considerable amount of work has been done on the oxidation-reduction equilibria of metal ions dissolved in alkali-metal borate glasses. Dissolved in these glasses, ferrous oxide is colourless, ferric oxide is yellow, and certain mixtures of the two are blue.[42] The spectral transmittance of borax glass containing dissolved iron has been measured.[39] Iron is in the trivalent state in air-melted alkali-borate glasses.[330] Transmittance studies have shown two forms of iron to be present under oxidizing conditions and three forms under reducing conditions.[40]

A discussion of the relation of acid–base properties of borate glasses to the oxidation-reduction equilibrium of dissolved transition metal ions has shown that Cr^{6+}, V^{5+}, V^{3+}, Co^{2+} and Ni^{2+} can be used as colour indicators to study the acid–base character of the glass.[1081]

A study of the manganous–manganic equilibrium in lithium, sodium and potassium borate glasses showed that there is a linear relation between log[Mn(III)/Mn(II)] and the mole-% of alkali-metal oxide. The equilibrium also shifts toward the oxidized state with increased atomic weight of the alkali metal.[639] The changes in the absorption of Mn(III) in lithium, sodium, potassium, rubidium and cæsium borate glasses with change in the ratio alkali oxide: B_2O_3 has been studied.[638A] The Mn(II)–Mn(III) equilibrium is also affected by temperature and oxygen pressure.[43]

Divalent cobalt in alkali-metal borate glasses is predominantly octahedral at low-alkali concentrations; tetrahedral cobalt increases with increasing alkali-metal oxide concentration and increasing atomic weight of the alkali metal. In binary alkali-borate glasses, the alkali oxide concentration at which the formation of tetrahedral cobalt begins is 18 mole-% K_2O, 19 mole-% Na_2O and 22 mole-% Li_2O.[640] The cobalt ion is red in acidic alkali-borate glasses and blue at higher alkalinity.[121]

Nickel ion shows two colours, due to yellow Ni^{2+} and violet-purple NiO_4^{2-} ions.[121] Optical absorption spectra of alkali-metal tetraborate glasses containing nickel oxide have been obtained and interpreted in terms of glass structure.[80, 83]

The effects of temperature, composition and oxygen pressure on the oxidation-reduction equilibria of chromium in molten $Na_2O–B_2O_3$[609], and in molten $Li_2O–B_2O_3$ and $K_2O–B_2O_3$[360] have been studied. Cr(III) and Cr(VI) were shown to exist in complex forms.[576A] Colour transformation curves in sodium, potassium and lithium borate melts containing chromium oxide at 1100°C have indicated a colour change at 17·5 mole-% Na_2O, 8 mole-% K_2O and 46 mole-% Li_2O. The Cr(III)–Cr(VI) indicator is yellow in strongly alkaline melts and green in strongly acidic melts.[515] Absorption bands for transition-metal ions change markedly at 15% Na_2O.[41]

Electron paramagnetic resonance studies of Cu(II) in cæsium borate glasses have been made.[1249] In binary alkali-metal borate glasses the minimum ratio of Cr(VI) to total chromium was at 25–30% Li_2O, 10% Na_2O and 3–5% K_2O.[609] The availability of oxygen ions for bond formation, as measured by the Cr(VI):Cr(III) ratio corrected for oxygen pressure, showed a minimum in the Li_2O–B_2O_3 system which could be correlated with anomalies found in the glass. No such minimum was found in the K_2O–B_2O_3 system.[360]

In Na_2O–B_2O_3–CuO glasses, measurements of spectral transmissions at various Cu^+ and Cu^{2+} concentrations indicated that Cu^+ had no effect on the absorption. For equal amounts of Cu^{2+}, increasing boric oxide up to 80% increased the absorption in the red. Still more boric oxide decreased the red and blue absorption.[471] The blue colour due to Cu(II) deepens with increasing alkalinity and decrease in temperature.[44] Both Cu^+ and Cu^{2+} absorb in the ultra-violet region. When sodium chloride is added, a chloro-complex is formed, more easily with decreasing sodium oxide content, and the ultra-violet and near infra-red spectra change significantly.[1057] A theory has been proposed to explain the effects of oxidation, reduction and boric oxide content on the colour of sodium borate glasses in terms of structure.[178]

ELECTROLYSIS OF BORATE MELTS

By electrolysis of alkali-borate melts in which are dissolved metal oxides, with or without additional salts, various metals and compounds have been produced.[21] Production of the following materials has been investigated: copper (unsuccessful from borate melts)[27], boron[6, 20, 26, 27, 375], carbides[22, 28], tantalum[27, 516], titanium[27, 1039], tungsten from ore concentrates[49, 250, 689A, 934, 1000], tungsten[20, 27, 516, 689A, 1000, 1001], spinels of vanadium[19, 24], a variety of borides[20–1, 27–8, 1155], zinc[20], molybdenum[20, 27, 934, 1220], carbon, Fe_3C, WC[22, 27], W_2C[27], Mo_2C[22], MgO,V_2O_3 and $Li_2O,2V_2O_3$[24], ferric oxide, $4FeO,Fe_2O_3,B_2O_3$[25], MoB, WB, MoC, W_2C, WC, arsenic, MoS_2, WS_2[28], WFe_2, W_2Fe_3, Mo_2C, W_2C, MoAs, WAs, W–Sb and Mo–Sb alloys[27–8], germanium[23, 51, 98, 251, 689], Ge–Ni, Ge–Fe, Ge–Mn alloys[51], Ge–Sn and Ge–As alloys[50], Ge–W and Ge–Mo alloys[51], antimony[179A]; sodium ferrate[25]; iron oxides[25]; Mo_2B, MoB, WB, arsenides, arsenic, WAs, MoS_2, WS_2[27, 900]; W_2Fe_3[900], niobium[27, 516], thorium[27, 516], zirconium[27, 294] and boride films on steel.[95A, 572, 637, 1024, 1086] B_2O_3:M_2O molar ratios of 2·5 to 12 are preferred for electrolytic boriding of metals.[1019] Electrolysis of alkali borates containing germanium dioxide produced unsatisfactory alloys, which contained boron.[48] Electrolysis of antimony oxide in fused borax produced antimony metal[179A, 900] but electrolysis of vanadium pentoxide in borax produced lower vanadium oxides rather than vanadium metal.[747] Borax or other borates, melted with boric acid, alumina and cryolite or other fluoride at 790–880°C forms an electrolyte for the production of aluminium.[1009] At 1100°C, drops of Ni_3S_2 and Cu_2S in a melt of 27% Na_2O and 73% B_2O_3 moved toward the anode; drops of copper moved toward the cathode.[395]

Boride films on tungsten, molybdenum, nickel, cobalt, tantalum, rhenium and iron were made by treating these metals with molten borax and B_4C.[572] Metal surfaces (including steel), have been borided in a fused-salt bath containing borax and carborundum.[927A, 1179]

OTHER ELECTRICAL PROPERTIES

From measurements on the cell Ni | NiO-molten $Na_2B_4O_7$ | O_2(Pt) at 800° and 900°C, thermodynamic functions of nickel oxide dissolved in fused borax have been determined.[611] Voltammetry and chronoamperometry studies have been made in carbonate–borate melts.[648A]

By means of e.m.f. measurements with platinum–oxygen electrodes, the activity and activity coefficients of lead oxide and bismuth oxide were evaluated in molten borax at 780°–920°C[203, 206, 1162] and in molten dipotassium tetraborate at 850°C.[326] The activity coefficients have also been evaluated by means of concentration cells.[612]

Polarographic studies of the oxides ZnO, GeO_2, MoO_3, Cr_2O_3 and WO_3 dissolved in molten borax have indicated that ZnO, GeO_2 and MoO_3 were reduced directly to

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metal by electrolysis.[762] Polarographic studies of the following oxides in fused borax have been reported: MgO, SrO, BaO, Al_2O_3, Cu_2O[404], ZnO, Cr_2O_3[205,404]; Fe_2O_3, CoO, NiO[200,204–5,404]; CuO[199,201,205]; CdO[199,201,205]; SnO_2[200,205]; GeO_2, Sb_2O_3, Bi_2O_3, MoO_3, WO_3.[205] Polarographic investigation of tin dioxide, antimony trioxide and bismuth trioxide in fused borax indicated that complex ions were formed in the melt[377] and that the metals could be determined by the polarographic method.[378]

Potentials of galvanic cells consisting of various oxides in contact with fused borax have been measured and discussed from a theoretical viewpoint.[651] Decomposition potentials of oxides dissolved in molten borax were determined at 840°C, leading to the following electrochemical series: Na, Cr, Mo, Fe, Mn, W, Zn, Sb, Ni, Sn, Cd, Bi, Tl, Co, Pb, Cu, Ag.[202] Heats of formation show that these oxides dissolve in molten borax with evolution of heat.[202]

For titanium dioxide and molybdenum trioxide in molten borax the decomposition potential was found to decrease with increasing concentration.[761] A study of the decomposition potentials suggests that in these electrolyses the primary process is the reduction of titanium or molybdenum oxides rather than the reduction of sodium, but that in the electrolysis of tungsten trioxide, sodium is formed, together with tungsten.[761]

The properties of the platinum in oxygen | Ca-stabilized ZrO_2 | salt melt electrode system in sodium metaborate have been compared with the properties of this electrode in other fused salts.[209] Dissociation and polarization potentials were determined at 900°C in the molten systems $Na_2B_4O_7$–NaF, $NaBO_2$–NaF and Na_3BO_3–NaF, and also in these systems with added zirconium dioxide. When zirconium dioxide was present, the dissociation potential was 0·6.[294]

The potentials of galvanic cells consisting of oxides in contact with molten borax and of borax in contact with window-glass melts have been studied.[651]

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SECTION A10

PREPARATION AND PRODUCTION OF ALKALI-METAL BORATES

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INTRODUCTION

The alkali-metal borates cover a wide range of compositions of the general formulation xM_2O,yB_2O_3,zH_2O, one of the features of the series being the readiness of boric acid to form numerous 'polyborates', the chemical authenticity of some being in doubt. Methods of preparation follow generally the fundamental acid–base reaction to form the appropriate salts, but derived and other methods have been known for many years. They are described in Mellor[1], by Kemp[2] and by Nies[3] (see also section A9), which reviews also contain extensive bibliographies (see also Yilmaz[4] and Menzel[5]).

The manufacture of alkali-metal borates is almost confined to the sodium salts, with minor activities in potassium, and to a lesser extent lithium. The sodium salts have an important and varied place in industry, and the quantities produced annually are very substantial and growing.[6] However, their manufacture is generally concentrated in a few large producers, and for this reason the literature on the chemistry of the processes and the detailed technology involved is relatively sparse.

This text will deal with the preparation and manufacture (where appropriate) of each individual borate in sequence under section headings for borates of lithium, sodium, potassium, rubidium and caesium, respectively.

LITHIUM BORATES

Lithium Tetraborate, $Li_2O,2B_2O_3,3H_2O$

This compound has been prepared on a commercial scale by direct reaction of lithium hydroxide and boric acid[7], a slurry of the two materials being heated to 90°–100°C to remove excess water formed by the reaction and then seeded to promote crystallization, which is followed by slowly cooling to 40°C to avoid formation of the di- or octa-hydrate. The exact degree of hydration of lithium tetraborate is in some doubt, both tetrahydrate[211] and trihydrate[212] being reported for crystals obtained from aqueous solution. Calcination at 400°–600°C will produce the anhydrous product. Direct production of the anhydrous material can also be effected by heating a mixture of lithium hydroxide and boric acid[8] gradually to 550°–650°C, sufficient lithium borate being recycled to prevent sticking and balling of the product. Lithium chloride has also been used for a fusion preparation.[10]

Lithium Metaborate, Li_2O,B_2O_3

This salt may be anhydrous or have $16H_2O$. According to Le Chatelier (ref. 1, p. 65), anhydrous lithium metaborate can be prepared by direct fusion of the stoichiometric quantities of lithium carbonate and boric acid or oxide; the hexadecahydrate is obtained by dissolution in water and controlled crystallization.

Refs. p. 510. Literature coverage is up to 1972

SODIUM BORATES

Basic Sodium Borates

A number of basic salts of the general composition $x\mathrm{Na_2O},y\mathrm{B_2O_3},z\mathrm{H_2O}$ have been reported[1–2], for example with $x:y = 3:2$, $5:2$, $3:3$ and $2:1$.

Sodium Metaborate

(Otherwise Sodium Diborate.)

This salt exists as several hydrates of the general composition $\mathrm{Na_2O,B_2O_3,}z\mathrm{H_2O}$.

SODIUM METABORATE OCTAHYDRATE, $Na_2O,B_2O_3,8H_2O$ OR $NaBO_2,4H_2O$

This, the normally available commercial form of this product, is produced by crystallization from an aqueous solution containing equimolar proportions of sodium hydroxide and borax below 30°C. Benedikt[1] produced triclinic crystals of this salt by concentrating a boiling solution and leaving it to crystallize over concentrated sulphuric acid. Manufacture by direct admixture of the necessary constituents, using borax penta- or deca-hydrate with sodium hydroxide dissolved in just enough water to furnish the composition desired, is described in a patent by Seibert.[12] Various methods also exist for the direct preparation of metaborate solutions from sodium or calcium borate minerals.[13–17] Sodium carbonate or bicarbonate may be used instead of the hydroxide. Some processes involve fusion prior to aqueous extraction.[15–16, 141]

SODIUM METABORATE HEXAHYDRATE, $Na_2O,B_2O_3,6H_2O$

Claimed to have been made by Berzelius as a confused mass of crystals by melting the octahydrate in its own water of crystallization and cooling the product to 0°C, can also be manufactured as a stable product by the direct addition of a sodium hydroxide spray of the correct composition to an agitated bed of borax pentahydrate.[18]

SODIUM METABORATE TETRAHYDRATE, $Na_2O,B_2O_3,4H_2O$

Also available commercially and may be obtained by direct crystallization from the metaborate solution at temperatures in excess of 55°C. It may also be prepared by vacuum dehydration of the octahydrate. Benedikt[1] prepared crystals of this product by fusing 1 mol of the octahydrate with 2 mols of sodium hydroxide and allowing the aqueous solution to crystallize.

LOWER HYDRATES OF SODIUM METABORATE

Various commercial processes exist for the preparation of metaborates of lower hydration by direct admixture and heating of the dry constituents, products corresponding to various hydrations (between 2 and 4) resulting.[19–20]

The monohydrate, $\mathrm{Na_2O,B_2O_3,H_2O}$, is reported to be formed by dehydrating the tetrahydrate, by crystallizing highly alkaline solutions above 40°C, or by seeding techniques.[2–3]

Sodium Tetraborate

(Otherwise Borax.)

Sodium tetraborate exists in several forms of the general composition $\mathrm{Na_2O,\text{-}2B_2O_3,}z\mathrm{H_2O}$, and is the best known of all the alkali-metal salts of boric acid.

SODIUM TETRABORATE DECAHYDRATE

Commonly known as 'borax' or 'decahydrate borax', this is the principal form of sodium tetraborate, being the stable modification under normal atmospheric conditions; it is comprehensively dealt with in Mellor[1] and Kemp.[2] There are four well-defined general methods of manufacture of borax, and a number of miscellaneous methods; these are dealt with in successive sections below. A general review up to 1931 was given by Santmyers[24]; other reviews are given by Dingley[25], Manning[26], Berlin[27] and Kitchen.[28]

Manufacture from Boric Acid

This method, described by Mellor[1], by Sborgi[30], and by Donato[31], has commercial application where boric acid occurs naturally, and where it is convenient to extract boron values from ores as boric acid, rather than as sodium salts. The preferred method is the reaction of alkali, usually sodium carbonate in hot aqueous solution, with the boric acid, the alkali being 1–5% in excess over theoretical (Dolley[32]). The resulting liquors may be treated with a variety of chemicals in small quantity to remove undesirable impurities, such as organic matter, iron, arsenic and other trace elements (Campbell[33–4]; Nies[35]; Taylor and Haber[36]; Kuhnert[37]; Schering-Kahlbaum A.-G.[38]; U.S. Borax and Chemical Co. Ltd.[39]; Nies and Kendall[40]; Kelly[41]), or electrolyzed (Penland[42]); it is then filtered to remove insolubles and crystallized by any of the conventional techniques. Those known to be in use include vacuum crystallization (Burke, Allen, Peet, Ritchie and Gale[44–5]; Burke[46]), agitated forced cooling at atmospheric pressure (Allen, Gale and Ritchie[47]), and natural cooling under static conditions (e.g., Watterson[48]). The last method produces relatively large masses of crystals, whereas the other methods in general use provide small discrete crystals of varying small sizes (known as granules), depending upon the conditions of manufacture and the equipment used.[22, 49–51] Various substances have been suggested as 'promoters' of crystallization, notably sodium nitrate.[52] The mother liquor is separated from the crystallized borax by natural drainage in the case of crystal, but usually by mechanical means such as a hydroextractor in the case of granular material. The liquor is sometimes discarded; it may be used as a re-cycling mother liquor, or evaporated to produce a further yield of borax, depending upon manufacturing circumstances. The de-watered borax is then dried, either naturally under suitable ambient conditions, or more usually in a hot-air stream in a conventional commercial drying plant. Care must be exercised in operating such equipment, as borax is somewhat temperature-sensitive even below 100°C and partial dehydration may occur, leading to a product slightly deficient in water and possibly liable to cake on storage (Burns[53], Schmitt[54]). The above-described methods are normally used in all commercial operations, whatever the source of borax liquor. Alternatively, a modification of the ammonia–soda (Solvay) process was proposed by Dresel and Lennhoff[55], in which the reaction $(NH_4)_2B_4O_7 + NaCl \rightarrow Na_2B_4O_7 + 2NH_4Cl$ was used, the ammonium borate being formed by the interaction of ammonia and aqueous boric acid. This system has been systematically studied by Sborgi and Franco.[56] Recent methods have also been described for the manufacture of borax by reaction of a sodium source (such as the hydroxide or bicarbonate) with ammonium borate solutions, the ammonium borate being thermally decomposed in a distillation column.[21]

Manufacture from Naturally Occurring Sodium Borate Ores

The principal naturally occurring sodium borate ores are tincal, $Na_2O,2B_2O_3,10H_2O$ and kernite $Na_2O,2B_2O_3,4H_2O$, which usually occur as relatively pure salts mixed with clays or shales, and in which the primary problem is the separation of the undesirable insolubles prior to the working up of the pure borate by methods such as those described in the previous section. A wide variety of methods for this primary separation has been proposed:

1. Digestion of the crude ore with water or mother liquor, with or without previous grinding, at normal or elevated pressures, at temperatures between 100°C and 400°C.[57–65] This type of process is currently used by U.S. Borax.[6, 29]

2. High-intensity magnetic separation.[66, 67]
3. Partial dehydration of ore, grinding and screening before aqueous extraction.[68]
4. Froth flotation.[69–71]
5. Treatment with excess alkali to form the more soluble metaborate prior to separation[73]; a slight excess of alkali is usually provided in the borax liquor to be worked up.[74] (The equipment used for separating the insolubles from the borax solutions is diverse, and is described in Section A3 of this Supplement.)

Manufacture from Natural Brines or Salt Lakes

A major naturally occurring source of sodium borate is in the brine liquors of certain partly dried-up salt lakes, notably Searles Lake and Owens Lake in California, where the borate is a minor but substantial constituent. The general method of recovery of borate (and other salts) is by fractional crystallization of the brines, which may or may not be treated with various other materials, with or without partial evaporation. There is extensive literature on these processes, which are reviewed.[6, 29, 75–9, 118] Process details have been described in patents.[80–100] Treatment of the brines with sulphuric acid (to increase borate solubility compared with potassium chloride[101], or to increase phosphate solubility compared with borate[102]), sulphur dioxide[98, 103, 107], sodium hydroxide[104], or sodium bicarbonate[105], is claimed to improve various salt separations. The effect of alkalinity on the crystallization of the brines was discussed by Wells.[106] Directly or indirectly altering the sodium bicarbonate/carbonate ratio in brines containing sodium carbonate gives improved means of separating borates from the other salts present.[107–8] Removal of small quantities of silica is achieved by sodium aluminate.[109] Use of calcium or magnesium borate or sodium metaborate is proposed for removal of carbonate[110] or phosphate.[111] Flotation methods of separating mixtures of salts are described.[113–16] Separation of lithium salts and borax from brines has been described.[117] Lime has also been used to treat magnesium-containing brines, the boron values being precipitated on magnesium hydroxide.[119] Ferric oxide and chromic oxide gels have been claimed to be effective in recovering boron values from the brines.[112]

More recently, processes have been developed using liquid/liquid extraction techniques to recover boron values from alkaline brines.[120–4] All or part of the liquid used for extraction forms complexes with the borate ions. The borate complex may be insoluble, when it is separated, or it may be recovered from the liquid extract as boric acid after treatment with mineral acid (usually sulphuric) and the boric acid then further refined as described above. The materials used for complexing include a wide range of polyols, and they may be used in conjunction with other organic liquids (usually kerosine) to act as carriers. Development of the techniques has revived interest in the extraction of boron values from brines weaker than those usually thought commercially workable; in particular, the ocean as a source of borates is now receiving renewed attention.[125] Earlier work in this field was concerned with concentration by evaporation[126], sorption on calcium or magnesium compounds[127], or removal from acidified brines by using aliphatic alcohols.[128] Methods are also described for the separation of borax from mixed saline deposits as obtained from the Ladakh area of Kashmir.[180] A permeable cell for the separation of borax from solution has been patented.[209]

Manufacture from Other Naturally Occurring Borate Ores

The calcium and sodium calcium ores such as colemanite, pandermite and ulexite have long been used as raw materials for borax production, but are now of less importance than formerly following major discoveries of relatively pure sodium borate deposits in California in 1927. They can be converted to borax by the action of sodium carbonate/bicarbonate as described in Mellor[1], and by Wood.[129] Yields in excess of 90% are obtainable by careful pH control.[58] Sodium pentaborate can be made directly from ulexite.[218] Modifications of the methods include the use of calcined colemanite[130,216] and use of continuous counter-current aqueous or aqueous-alkali extraction.[131–3, 215] Sulphur dioxide has been used to decompose calcium ores[134–5], as have ammoniacal solutions (to form ammonium borate, which can then be converted to appropriate sodium salt).[136,210] Use of water alone to extract boron values from calcium borates has been suggested, but seems likely to be only of academic interest.[137] The results are also of doubtful validity.

More complex borates, sometimes with very low boron values, have been used to produce borax, usually via boric acid as an intermediate. The borates used are often magnesium-containing, and may also contain combined silica. The methods employed are often highly involved and usually designed in detail to suit the available ore supply, which may vary considerably in the content of gangue impurity. Hydroboracite ($CaO,MgO,3B_2O_3,6H_2O$) and ascherite ($2MgO,B_2O_3,H_2O$) are the best known magnesium containing ores used for this purpose. An electrolytic aqueous solution method, whereby sulphuric acid produced from magnesium sulphate dissolves suspended mineral, is described.[138] Decomposition of hydroboracite by sodium sulphide yields sodium metaborate as a first step[139]; this method may also be applied to ascharite.[140] Other methods using ascharite are fusion with sodium carbonate and sodium hydroxide followed by treatment of the aqueous solution with various materials, such as boric acid and magnesium sulphate liquor[141] or carbon dioxide.[142] The ore may also be roasted and then extracted with aqueous sodium bicarbonate.[143] Kotoite, $Mg_3B_2O_6$, has been worked up by either acid or alkali extraction[146], and further comment on this and similar ores is available.[23, 147] Naturally occurring borosilicates such as datolite and tourmaline have also been used as sources of boron. The ore is calcined and extracted with aqueous alkali[148–51], calcined in admixture with limestone, the product being decomposed by simultaneous action of soda and carbon dioxide[152], or finely ground and leached with carbonic acid.[217]

Miscellaneous Methods of Preparation

Sodium pentaborate may be converted to borax and boric acid by aqueous reaction with sodium chloride and ammonia.[153] Double decomposition of ammonium borate, $(NH_4)_2B_4O_7$, and sodium sulphate also produces borax.[154–5] An interesting method for all the alkali–metal borates is the ignition of boric acid with an appropriate salt; for borax, sodium chloride is used at 800°–850°C.[10, 156] Potassium pentaborate yields borax when treated with sodium bicarbonate, carbonate or hydroxide.[160] Removal of borax from nitrate solutions is carried out by precipitation with lime and magnesia.[161] Borax may be separated from sodium sulphate by conversion into the more soluble metaborate and filtration.[162] Use of strongly alkaline anion exchangers as a method of recovery from solution is suggested.[25, 163]

SODIUM TETRABORATE PENTAHYDRATE

This hydrate, $Na_2O,2B_2O_3,5H_2O$, is a metastable form of borax, but it is an important article of commerce as a readily water-soluble salt with a higher boric oxide content than the decahydrate. It may be prepared by crystallizing borax solutions at temperatures above 60°C, and it is sometimes produced as an intermediate in working up various borate ores. Details are given by Kemp.[2] Control of the size of pentahydrate crystals has been described in a patent.[164]

SODIUM TETRABORATE TETRAHYDRATE

Kernite is the naturally occurring form of this hydrate, $Na_2O,2B_2O_3,4H_2O$, which is the stable hydrate above 58·5°C.[2] It is not normally formed by crystallization at such temperatures, the metastable pentahydrate being formed instead. The tetrahydrate may be produced, however, by maintaining a concentrated solution of borax at 84°–100°C for long periods, and adding kernite seed, when the sparingly soluble tetrahydrate eventually separates out.[165] Formation of the tetrahydrate has been known in borax process plant operating under favourable conditions for its formation; the slow build-up inhibits heat transfer and sometimes causes mechanical problems. Removal is troublesome owing to its very low rate of solution in water.

SODIUM TETRABORATE DIHYDRATE

Little is known of this alleged compound $Na_2O,2B_2O_3,2H_2O$.[1–2]

SODIUM TETRABORATE MONOHYDRATE

Few details are available, but the preparation of a crystalline form of $Na_2O,2B_2O_3,H_2O$ has been described.[2–3, 166] An amorphous form is also known and may be obtained by heating the decahydrate at 180°C to constant weight.[167]

ANHYDROUS SODIUM TETRABORATE

Dehydration of borax decahydrate by heating is a stepwise process, accompanied by intumescence (see below) and not all of the water is eliminated until a temperature of at least 300°C is reached.[194] In fact, about 1% is retained until the material is melted. The anhydrous borax, or 'borax glass', of commerce is made at the rate of several hundred thousand tons per annum by fusion in large furnaces.[29] As its name implies, the chilled product is glass-like in appearance and is largely amorphous; it can be induced to crystallize, however, by prolonged annealing or by seeding.[2] The glass melts at about 741°C and readily supercools. Temperatures in excess of 750°C are necessary to produce it and much effort has been expended in fusion equipment development, with especial reference to minimizing the attack on furnace refractories.[168–73] Methods have been devised for keeping the borax away from the furnace walls.[173] As the product is usually required in granular form, considerable attention has also been given to ways of facilitating comminution. Rapid chilling can produce fine granules.[158–9] Removal of the fused mass from the furnace hot-zone immediately upon fusion and before the last traces of water have been eliminated (its slow final release producing a porous material) was the subject of an early patent.[193] More practically, methods have been developed for chilling the melt into readily crushed sheets or thread, desirably avoiding the production of excessive amounts of fine particles.[174–7] The production of small crystals as opposed to vitreous particles has also been described[178–9, 181] and a process developed for separating the vitreous and granular forms.[182]

Although the anhydrous borax of commerce is the glassy form, attempts have been made to produce it by lower-temperature methods (i.e. below fusion point). Patents describe stepwise dehydration in a multistage fluidized-bed drier process reaching 220°–700°C in the final stage[43]; and spraying borax solution on a particulate agitated mass of anhydrous material heated at 400°–700°C.[145]

INDETERMINATE HYDRATES OF SODIUM TETRABORATE

Many hydrates of indeterminate degree of hydration, but usually containing between 0 and 5 mols of water per mol of $Na_2B_4O_7$, have been reported. Some, including 'calcined borax', are commercially available and they are also used as feedstock in the production of anhydrous borax by fusion. Such a product contains typically 20–22% of water.[189] Decahydrate borax intumesces when heated and the solid product which remains after this initial melting and before fusion into a glassy liquid is of this lower hydrate nature. So-called non-vitreous desiccated borax was produced from hydrated borax by heating at 360°C with continuous removal of expelled water.[190] Various methods of preparation by heating with hot gases below the melting point of borax were described in early patents[188–9, 191] and a procedure has been given for breaking up the cellular structure to give a product of higher bulk density.[192] A product of low bulk density is sometimes sought and more recently methods have been disclosed for the production of 'puffed' or expanded borax by heating the pentahydrate in a rotary oven[157] or fluidized bed.[72] Material with a bulk density as low as 0·05 g cm^{-3} can be obtained in this way. The high surface area of the product facilitates its use as a carrier for the minor ingredients of borax-based detergent compositions and similar products.[195–6] Partially hydrated sodium borates of other than the exact tetraborate ratio have been prepared by agitating mixtures of anhydrous borax and hydrated borax particles at 70°–115°C in a suitable tumbler drier.[11] The calcination of metallic salts, with particular reference to borax, was reviewed by Rakuzin[183], who developed the dehydration theme further in his own experimental work.[184–7] Cold 95% alcohol, which dehydrates sodium sulphate, had no effect on decahydrate borax[184], but refluxing for 2 hours removed 6 mols of water[186] and ultimately a further mol.[187] Treatment of decahydrate borax with cold dry air had no effect, whereas standing over dry sulphuric acid reduced it to the pentahydrate.[185] A product with 2–4 mols of water of crystallization can be obtained by heating a saturated aqueous borax solution containing borax crystals at 120°–130°C until the desired level of dehydration is achieved.[194] A dehydration method based on azeotropic distillation from a suspension of borax crystals in an organic solvent has been patented.[144]

Sodium 2:5 Borate

Known as 'Auger's borate' after its discoverer, $2Na_2O,5B_2O_3,5H_2O$ is formed by treating the stoichiometric quantities of Na_2O and B_2O_3 in aqueous solution under prescribed conditions.[2]

Sodium 3:8 Borate

Little is known of an alleged decahydrate, $3Na_2O,8B_2O_3,10H_2O$, often called 'Suhr's borate'. Comment[3] suggests that it is possibly $2Na_2O,5B_2O_3,7H_2O$.

Sodium 1:3 Borate

This compound is reported, but only bare details are known.[2]

Sodium 1:4 Borate

Preparation of anhydrous $Na_2O,4B_2O_3$ by fusing a composition with the ratio $B_2O_3:Na_2O$ between 3·7 and 4·0 or less is described.[197–8] By controlling the cooling conditions a mainly crystalline form, as opposed to a vitreous product, is claimed. Some hydrated forms have also been reported.[2] A tetrahydrate marketed widely under the trade name '*Polybor*' is produced by spray drying a solution of the appropriate molar composition.[208]

Sodium Pentaborate (Sodium 1:5 Borate)

SODIUM PENTABORATE DECAHYDRATE, $Na_2O,5B_2O_3,10H_2O$

Prepared by Atterberg[1], who found that a solution of 1 mol of sodium hydroxide with 5 mols of boric oxide deposited small prismatic crystals of this salt. The salt is normally made industrially by dry mixing the constituents and heating. According to Nies and Taylor[199] it may be produced by heating a mixture of decahydrate borax and boric acid in a molecular ratio of 1 to 6 in a rotary drier at a temperature of 30°–38°C, and progressively increasing the temperature to 66°C, at which most of the water has been removed. Various other methods have been proposed for the direct production of this substance from boron-containing crude ores by their treatment with sulphur dioxide[200] or carbon dioxide[201], or soluble non-alkali-forming metal sulphates.[202]

SODIUM PENTABORATE OCTAHYDRATE, $Na_2O,5B_2O_3,8H_2O$

This compound has been claimed by Menzel[2], but has not been isolated. Several other hydrates have also been postulated.[2]

ANHYDROUS SODIUM PENTABORATE

According to Hackspill, Rollet and Andrès[204], anhydrous sodium pentaborate may be prepared by heating sodium chloride with boric acid at 100°–150°C in a current of steam. Small commercial quantities were offered in 1950, but the method of manufacture has not been published, and this material is not now available.

Sodium 1:6 Borate

Existence of such a compound is claimed, but little is known about it.[2]

POTASSIUM BORATES

Potassium Metaborate, K_2O,B_2O_3 or KBO_2

This is not a normal article of commerce. It has been prepared by Berzelius[1] by fusing equimolecular proportions of potassium carbonate and boric oxide or boric acid at a white heat, the product being dissolved with difficulty.

Potassium Tetraborate Tetrahydrate, $K_2O,2B_2O_3,4H_2O$

This compound has been prepared by May from borax solutions by the addition of potassium chloride to crystallize potassium tetraborate isothermally from the solution, the interaction apparently being assisted by the presence of ammonia.[205] It is also obtained by direct aqueous reaction of boric acid and potassium hydroxide to give the 8 or 4 hydrate, and from borax and potassium chloride in a cyclic process in which the mother liquor is carbonated.[9, 206] It may be obtained by ignition of boric acid with potassium nitrate at 500°C, potassium chloride at 800°–850°C or potassium sulphate at 1000°C.[10] It may also be produced along with borax by the action of sodium bicarbonate, carbonate or hydroxide on potassium pentaborate.[160]

Potassium Pentaborate

The octahydrate, $K_2O,5B_2O_3,8H_2O$, is commercially available and may be prepared by the carbonation of a solution of borax and potassium chloride, the reaction proceeding according to the equation:

$$4KCl + 5Na_2B_4O_7,10H_2O + 6CO_2 \rightarrow 2K_2B_{10}O_{16}8H_2O + 6NaHCO_3 + 4NaCl + 31H_2O$$ [206–7]

It may also be made according to Gale[203] by direct crystallization from a mixture of potassium chloride, boric acid and a basic sodium borate, the proportions being such as will be substantially equivalent to the potassium pentaborate desired. Alternatively, it can be prepared by direct crystallization from a boiling aqueous solution of potassium hydroxide saturated with boric acid. An earlier patent had described a process involving potassium chloride, boric acid and ammonia.[214]

Anhydrous potassium pentaborate may be prepared in the same manner as anhydrous sodium pentaborate.[204]

A crystalline compound of composition $K_2HB_5O_9,xH_2O$ has been prepared from potassium hydroxide and boric acid.[213]

RUBIDIUM BORATES

Reischle[1] prepared anhydrous rubidium tetraborate $Rb_2B_4O_7$ by direct precipitation from alcohol solutions of rubidium oxide and boric acid. The hexahydrated form $RbB_4O_7,6H_2O$ was also prepared by Reissing and Reischle[1], by dissolving molar quantities of boric acid and rubidium carbonate in boiling water. The pentaborate of rubidium has also been prepared by Rosenheim and Leyser.[1]

CÆSIUM BORATES

Reischle[1] also produced cæsium hexaborate, $Cs_2O,3B_2O_3$, from alcoholic solutions of cæsium oxide and boric acid.

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Ignition of boric acid with rubidium or cæsium chloride at 300°C gives the corresponding borate.[10]

Cæsium metaborate $Cs_2O,B_2O_3,7H_2O$ may be prepared from cæsium nitrate. Cæsium diborate and pentaborate have been reported.[3, 67]

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SECTION A11

BORATES OF COPPER AND SILVER

BY E. E. EMMETT

This Section covers the borates of the copper–silver–gold group. There is no report so far of the existence of a borate of gold.

BORATES OF COPPER

A copper borate occurs naturally in double-salt form as the mineral bandylite, $CuO,B_2O_3,CuCl_2,4H_2O$, which is of interest because of its crystallo-chemical relation to teepleite, $Na_2O,B_2O_3,2NaCl,4H_2O$. The crystal structure of bandylite has been the subject of considerable investigation.[1–5] It is tetragonal and each boron atom is surrounded tetrahedrally by 4 hydroxyl groups, no H_2O groups occurring in the lattice. It is reported to be decomposed by water, yielding a copper borate of unspecified composition, which appears as a green insoluble residue.[1]

Anhydrous Copper Borates

CuO,B_2O_3. Anhydrous 1:1 copper borate, CuO,B_2O_3, is prepared by fusion of cupric oxide with excess of boric oxide[6, 51]; the product is stated to be blue when prepared in this way, the latter reference quoting preparation at 950°C. A green compound with an unidentifiable *X*-ray powder pattern has, however, been obtained from similar melts at 650°C[7]; see also ref. [51]. Other workers report that a green product is obtained at 850°C, whereas it is blue if prepared at 1000°C.[8] The varying colours reported suggest the presence of differing amounts of Cu(I) in the lattice. CuB_2O_4 crystallizes in the tetragonal system, with all B atoms tetrahedrally coordinated and each Cu atom surrounded in a planar-square coordination by 4 O atoms.[52] *d* (calc.) = 4·02. The dissociation pressure of CuO,B_2O_3 at temperatures used in its preparation is considerable, e.g., at 860°C the pressure of oxygen in equilibrium with the melt is reported to be 237 mm Hg.[9]

$$12(CuO,B_2O_3) \rightarrow 2(3Cu_2O,B_2O_3) + 3O_2 + 8B_2O_3$$

Recent work has shown that green $3CuO,B_2O_3$ is formed as a result of a solid-state reaction between CuO and CuO,B_2O_3 at 800°C.[51] From earlier information it would be expected that the higher the temperature used for the preparative fusion the richer the product would be in Cu(I). If this were the case, the latter products would be greener than those obtained by low-temperature fusions. Thus it seems that where conditions of preparation are not clear, the reported composition and homogeneity of the products must be viewed with scepticism. It appears that pure CuO,B_2O_3 would probably best be obtained by fusion under an atmosphere containing the appropriate oxygen pressure required to suppress its decomposition.

In addition to the above-mentioned methods CuO,B_2O_3 has been prepared by heating an intimate equimolar mixture of cupric sulphide and borax.[10] In a study of the reduction of CuO,B_2O_3 in a stream of hydrogen at 500–750°C, it was found that the reaction follows the course:

$$CuO,B_2O_3 + H_2 \rightarrow Cu + B_2O_3 + H_2O$$

Refs. 518. Literature coverage is up to 1971

and that hydrogen in excess of the theoretical amount is used. At 500°C only the theoretical amount of hydrogen was required for the reduction; however, as the temperature was increased there was parallel increase in the extra hydrogen consumed, reaching a limiting value at 700°C of one g-atom of hydrogen per mole of CuO,B_2O_3. It is suggested that this consumption of excess of hydrogen may be due to activated adsorption.

$CuO,2B_2O_3$. A 1:2 copper borate, $CuO,2B_2O_3$, has more recently been prepared by pyrolysis of the compound $[Cu(NH_3)_4]B_4O_7,6H_2O$ under reduced pressure[11]; the pyrolysis is not accompanied by volatilization of boric oxide. This confirms earlier work by Pasternack reported in Mellor.[6]

Physical data for copper borate systems are not readily available. *X*-ray powder diffraction data for an unspecified copper borate have been reported; no preparative details or stoichiometry are given, although it is almost certainly an anhydrous compound.[12] Infra-red absorption studies on several borates, including a copper borate formulated as $3CuO,2B_2O_3$, have been used to determine the structure of the borate ion in the lattice.[13, 51] The B–O bond is apparently not localized, as is the B–Cl bond in boron trichloride.[13] Other workers report absorption in the far infra-red, where one absorption band is said to be the same as that found for cupric oxide.[14–15] In a study of paramagnetic resonance absorption, CuO,B_2O_3 revealed no absorption at room temperature, with magnetic fields of up to 15,000 gauss.[16]

Cu_2O,B_2O_3 and $Cu_2O,2B_2O_3$. A relatively recent phase study of the Cu_2O–B_2O_3 system has demonstrated the existence of the compounds $CuBO_2$ and CuB_4O_7.[53] This system includes 10–40 mol-% Cu_2O. From 20–40 mol-% Cu_2O the new composition CuB_4O_7 exists, in two modifications. It melts congruently at 1060°C. CuB_4O_7 crystallizes in tetragonal symmetry, is dark blue and d (expl.) $= 3{\cdot}71$. $CuBO_2$ forms at 70 mol-% Cu_2O and melts congruently at 1075°C. $d = 4{\cdot}64$. D.T.A., *X*-ray and infra-red absorption studies were reported.

Hydrated Copper Borates

Studies of hydrated copper borate systems have been hampered by the fact that double-decomposition preparation methods lead to colloidal or near-colloidal precipitates, the compositions of which are difficult to determine unambiguously.[17–18] Much of the recent work has been done by Boiko[19–20], and by Kešāns and Khadorchenko.[21–2] The former obtained a hydrated 3:2:3 copper borate, $3CuO,2B_2O_3,3H_2O$, from solutions of cupric chloride and borax. Similar borates, with 1–5 moles of water, were prepared from solutions of cupric sulphate, cupric hydroxide and borax. Storage of these compounds for two years, however, resulted in conversion into the 2:1:1 compound $2CuO,B_2O_3,H_2O$.[19–20]

In a study of the system $Cu(OH)_2$–H_3BO_3–H_2O, it was found that three metastable hydrated copper borates can be obtained, the ratios of $CuO:B_2O_3:H_2O$ being 2:1:15, 3:2:6 and 2:1:17.[21] Which of these is formed depends on the temperature of the solution, and in each case the product is formed in dispersed condition. When dried, these precipitates yield glass-like phases. In contact with the mother liquor for periods of up to five years, the metastable hydrates change to a stable form of composition $2CuO,B_2O_3,3H_2O$, which when dried forms a powder, suggesting micro-crystallinity.[21]

A hydrate with yet another stoichiometry is reported by Švarcs.[23] This material, formulated as $CuO,B_2O_3,2H_2O$, was studied to determine the effect of particle size on its dehydration. It was found that the dehydration temperature increases with both particle size and storage time, the latter effect being more apparent with smaller particles.

The fact that the precipitation of hydrated copper borates results in colloidal precipitates of variable composition, which change to a stable form only after some considerable time, suggests that the initial step is formation of an adsorption complex of borate ions or boric acid with precipitated copper hydroxide, which slowly changes into the hydrated copper borate. The solutions usually involve alkali–metal borates, and so the pH is relatively high. This sequence is further supported by the fact that boric acid can be leached from the 'metastable hydrates' initially formed.[24]

In the determination of the solubility products of borates of copper, the systems copper oxalate–boric acid–water, $CuOHBO_2$–boric acid–water and Cu^{2+}–$HSal^-$–boric acid, have been studied (H_2Sal represents salicylic acid).[25] The author reports the formation of the complex anions $[Cu(BO_2)_3]^-$, presumably $[Cu(BO_2)_3H_2O]^-$, $[Cu(BO_2)_3HSal]^{2-}$ and $[Cu(BO_2)_2Sal]^{2-}$; dissociation constants for these species are given.

Solubility products obtained are: $CuOHBO_2$ $5{\cdot}4 \times 10^{-18}$ and CuO,B_2O_3 $2{\cdot}90 \times 10^{-15}$. The former species would perhaps be better considered as $2CuO,B_2O_3,H_2O$, with presumably half the solubility product, i.e. $2{\cdot}7 \times 10^{-18}$.

Nearly insoluble copper borates are reported to be solubilized by steeping with aqueous zirconyl acetate and zirconyl ammonium carbonate at 25°C for 1–2 days.[26]

Copper borate has been successfully used as a catalyst, mixed with alumina, for the conversion of acetoxyacenaphthene to acenaphthylene.[27]

In agriculture, copper borates have been found effective in treating d'Anjou pears for Cork Spot disease[28], but the main effort in this field has been directed towards realizing its potential as a timber preservative.[24]

A complex copper borotungstate can be obtained by double decomposition of barium borotungstate and copper sulphate.[29–30] It forms a series of hydrates of general formula $Cu_5H_8[B(W_2O_7)_6]_2,nH_2O$, where $n = 57$, 63, 69, 74 or 77.[31] Aqueous solutions of these compounds are acidic, indicating that they are acid salts.

A compound designated copper sulphatoborate with formula $Cu[B(SO_4)_2]_2$ has been described.[32] It is prepared by interaction of copper sulphate, boric acid and sulphur trioxide; it is reported to be very hygroscopic and recrystallizable from sulphuric acid. The *X*-ray diffraction patterns of a series of these compounds suggest similar structures, and it is suggested that they are ionic with highly polymeric anions.

BORATES OF SILVER

Anhydrous Silver Borates

Until recently only one anhydrous silver borate had been definitely established, viz. the 1:4 compound, $Ag_2O,4B_2O_3$, which was obtained from boric oxide melts by the slow addition of solid silver nitrate.[33] The product appeared (at 570°C) as white crystals from a melt of the composition $Ag_2O,4B_2O_3$. The stoichiometry of this compound was confirmed by analysis. In both this work and that of Foex, who added silver oxide to boric oxide melts at 1200°C, there was found to be a limit to the solubility of silver oxide at 61% Ag_2O.[34–5]

Willis and Hennessy, in a thermodynamic study of the system, found a point of inflection in the chemical potential curve at a mole fraction of silver oxide of 0·2.[36] Taking the standard state of silver as a solid silver oxide, they estimate the free energy of formation of liquid $Ag_2O,4B_2O_3$ at 850°C to be $-17{\cdot}5$ kcal. The method used was to contain the melts in silver vessels, and analyze quenched material after equilibration at a particular oxygen pressure. On account of the use of silver vessels, the activity of the silver oxide in the melt was directly proportional to $p_{O_2}^{1/2}$. This method clearly gives an unambiguous estimate of the silver oxide content of the melt. It should be noted that earlier workers reported yellow glasses to be formed at higher silver oxide concentrations, suggesting the presence of free silver[33–5], but by use of an ultramicroscope it was established that the lemon-yellow glasses did not contain colloidal silver. It is clear that high oxygen pressures would be required to study the system at concentrations above 61% Ag_2O.

In a recent study of the anhydrous system, using a thermal analysis approach, Kocher and Sadeghi[37] isolated compounds of composition $Ag_2O,2B_2O_3$ and $Ag_2O,9B_2O_3$, as well as two crystalline forms of the 1:4 compound $Ag_2O,4B_2O_3$.[37] The 1:2 silver borate, $Ag_2O,2B_2O_3$, was obtained by crystallization at 500°C of its amorphous dihydrate. At 688°C this compound melted incongruently to give the β-form of $Ag_2O,4B_2O_3$, which occurs as large, beige, metastable crystals melting at 740°C. The α-form of this compound is reported to be the stable form, melting at 755°C; it occurs as fine needles, which are obtained only after prolonged annealing of the β-form at 600°C. The compound $Ag_2O,9B_2O_3$ is said to occur as fine, white crystals, melting at 683°C.

X-ray data are given for the two compounds, and it is evident that the data presented by a previous study refer to the β-form of $Ag_2O,4B_2O_3$.[38] In the previous work the silver borate was found to be monoclinic. This study was extended to include a solid solution of the same phase, wherein 40 at.-% of the silver atoms were substituted by sodium atoms. The resultant phase had cell dimensions only slightly different from those of the pure silver borate, indicating a structural relationship between $Na_2O,4B_2O_3$ and $Ag_2O,4B_2O_3$. The borate anion in the crystal was found to consist of two separate, identical, three-dimensional, interlocking networks. The units comprising these networks have previously been found in tri- and pentaborates.

Markin measured the electrical conductivity of silver borate glasses containing the alkali metal oxides Li_2O, Na_2O and K_2O[39–42], and found that there was a minimum in the conductivity curve in each system. In the case of sodium and potassium, this minimum is said to occur with a silver:alkali–metal ratio of approximately 1:4, whereas with lithium it is nearer to 1:2·3. In the same series of experiments, ion-displacement energies were found to be less than for the corresponding binary systems and were interpreted to indicate the formation of mixed borates.

Hydrogen reduction of $Ag_2O,2B_2O_3$ is reported to yield metallic silver quantitatively.[45]

Products with other reported compositions are obtained by double decomposition methods.[46] If free alkali is present, the precipitate is said to contain less B_2O_3; when free boric acid is present, a B_2O_3-rich precipitate is produced. In the absence of physical data for these alleged compounds of variable composition, their actual existence must be viewed with reserve.

Souchay reported a precipitate with a mole ratio of 1:1, viz. Ag_2O,B_2O_3, obtained from a solution of boric acid and silver nitrate to which sodium hydroxide solution was added. The amount of combined water was apparently not determined.[47] The compound is said to be reduced by hydrogen to metallic silver thus:

$$Ag_2O,B_2O_3 + H_2 \rightarrow 2Ag + B_2O_3,H_2O$$

Van Tiggelen *et al.*, in studies of reduction of silver salts by hydrogen, prepared a borate regarded as Ag_2O,B_2O_3 from silver nitrate and presumably excess of sodium metaborate, Na_2O,B_2O_3.[48] The precipitate was formed on quartz grains and purified by washing out the excess of sodium metaborate.

A borate used by Khundkar *et al.*, also in connection with hydrogen reduction processes, was obtained by the interaction of molar silver nitrate and saturated borax solution, and its stoichiometry was allegedly established by chemical analysis to be Ag_2O,B_2O_3.[49] These workers found that the reduction is accompanied by adsorption of the hydrogen, apparently on silver atoms at the surface of the solid.

It is interesting that workers examining the Ag_2O–B_2O_3 system, with or without water, have not reported any conclusive evidence for a 1:1 compound.[36–7, 43] Hence the existence of such a compound remains unconfirmed.

The 1:2 silver borate, $Ag_2O,2B_2O_3$, has been used in the study of the mobility of borate ions in solution.[50]

Hydrated Silver Borates

The ternary system Ag_2O–B_2O_3–H_2O has been recently studied by Sadeghi over the range 0–100°C.[43] Isotherms for the temperatures 0, 18, 30, 56, 78 and 100°C indicated the composition and range of existence of the compounds that occurred as phases stable at atmospheric pressure. In addition to Ag_2O and H_3BO_3, two solid-compound phases were involved in the solution equilibria. These were the 1:2:2

Refs. p. 518

and 2:5:5 hydrated silver borates, i.e. $Ag_2O,2B_2O_3,2H_2O$ and $2Ag_2O,5B_2O_3,5H_2O$. The isotherms were obtained by using the solubility method, and the solid phases were identified by *X*-ray diffraction of rapidly dried specimens. Thermogravimetric methods were also used to characterize these compounds.

This is the first reported observation of the formation of $2Ag_2O,5B_2O_3,5H_2O$; it was not indicated in the isotherms below 56°C, but in the higher temperature ranges it was more pronounced and was found to be stable up to 140°C. The minimum temperature of equilibrium stability in solution was apparently not established. Dehydration of this new compound followed a similar pattern to that of the analogous sodium salt, but the *X*-ray powder diagrams were found to be dissimilar.

$Ag_2O,2B_2O_3,2H_2O$ is an established compound, previously characterized as the precipitate obtained when silver nitrate is added to an aqueous solution of boric acid and borax, with $B_2O_3:Na_2O$ ratio exceeding 5:1.[44] It is only slightly soluble in water, but the solubility increases when boric acid is present.

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SECTION A12

BORATES OF GROUPS II, III, IV, VII, VIII (INCLUDING LANTHANIDES)

BY G. H. BOWDEN AND R. THOMPSON

BORATES OF GROUP II

General Properties

More is known about the borates of this group than any other except the alkali metals. The mineral borates of calcium and magnesium are widely distributed in nature and have been extensively studied both as the minerals themselves and as their derivatives. The anhydrous borates of Group IIa occur rarely as minerals, but have been investigated because of the interest in their effect on glass composition and more recently, in activated forms, in their use in phosphorescent materials.

Beryllium shows quite anomalous behaviour, as may be expected. Only one anhydrous borate is known and no hydrated borates have been synthesized under normal conditions of temperature and pressure. Anhydrous magnesium borates have rarely been studied in conjunction with calcium, strontium and barium; but the latter have been extensively compared. The $MO–B_2O_3$ systems[1] ($M = Ca$, Sr, Ba) show large areas of two-phase immiscibility[2] which may be homogenized by the incorporation of a few per cent of alkali oxide, etc. When this homogenization is accomplished it is then possible to compare certain properties of the melts. For instance, viscosities[3] and surface tensions[4] of the liquid phases have shown that they decrease in the order $CaO > SrO > BaO$ and that the densities, as would be expected, have the inverse relationship.[3] The systems $Li_2O–MO–B_2O_3$ have been investigated, and the properties of the glasses as well as the densities, refractive indices, chemical stabilities and thermal coefficients have been compared.[5] Physico-chemical properties of a variety of anhydrous alkaline-earth borates, such as the heat contents between 25° and 1100°C, heats of solution in 2N nitric acid, heats and entropies of fusion, and entropy changes over a range of temperatures have been determined.[6]

The interactions of various anhydrous alkaline-earth metaborates have been characterized by phase studies on a selection of their binary systems.[7] The infra-red spectra of the orthoborates have been compared.[8] Borates of the type $MSn(BO_3)_2$ have been shown to have dolomite structures.[9,10] Details of the formation and properties of alkaline-earth sulphato-borates have been recorded.[11] The general reaction of alkaline-earth borates of the form MO,xB_2O_3 (where $x = 1–5$) with triethyl or triphenyl boron and boron tribromide, to give triethyl or triphenyl boroxine, has been patented.[12] Alkaline-earth borates also react with hydrogen at 3–5 atm, with an alkali metal and silica to form borohydrides.[13]

Alkaline-earth borate phosphors activated with samarium[14–15], terbium[16], cerium[14], lead[17], bismuth and manganese[18] have been studied. Further reference to this subject is made under the particular borate involved or in the specific section on fluorescence. Alkaline-earth borophosphates of the general formula $2MO,B_2O_3,P_2O_5$, activated with bivalent europium have been studied in relation to their luminescence.[20]

The field of hydrated alkaline-earth borates has been extensively studied, by the Russians in particular, especially in a mineralogical context. This emphasis arose from the presence of large deposits of low-grade alkaline-earth borates in the U.S.S.R. and the difficulty of processing them. As there are no natural barium borates and few strontium borates it is significant that little Russian work on this subject is evident. Much recent work on these borates, and those of magnesium and calcium, at high temperatures and pressures has come from Lehmann in Germany. A good review of the Russian work on hydrated alkaline-earth borates is to be found in a paper by Kesans.[21] A more recent general review is by Nies and Campbell.[22]

All alkaline-earth borates are soluble to a slight extent, and all hydrolyse with the formation of boric acid and/or intermediate polyions. The following reactions have been suggested.[23]

(a) *Metaborates*

$$MB_2O_4,xH_2O + H_2O \rightarrow M^{2+} + 2OH^- + 2H_3BO_3$$

(b) *Triborates*

$$MB_6O_{10},xH_2O + H_2O \rightarrow \begin{cases} M^{2+} + B_6O_{10}^{2-} \\ M^{2+} + B_4O_7^{2-} + 2H_3BO_3 \\ M^{2+} + 2BO_2^- + 4H_3BO_3 \\ M^{2+} + 2OH^- + 6H_3BO_3 \end{cases}$$

The addition of alkaline-earth salts to boric acid lowers the pH sufficiently to permit direct titration of the acid.[24] Although there seems to be good evidence of alkaline-earth borate complexions to explain such a phenomenon, other work does not indicate that complex formation is responsible.[22]

Salts of the type $K_2O,M^{II}O,4B_2O_3,xH_2O$ (M^{II} = Ca, Sr, Ba) are formed[318] which hydrolyse to give monoborate ions (BO_2) and free boric acid; the degree of hydrolysis is self-compensating owing to the reverse effect of the formation of boric acid.[25]

It is interesting that among the alkali-metal compounds the 'tetraborates' $M^I_2B_4O_7,xH_2O$, where M^I = alkali metal, are the most stable borates; the same generalization does not apply, however, among the alkaline-earth borates and it is doubtful whether any compound of the formula $M^{II}B_4O_7,xH_2O$ has been characterized. A recent reference[26] quotes the formation of alkaline-earth tetraborates (and fluorides) by treating the metal with fluoboric acid and evaporating the solution; whether these conditions are suitable for the formation of hitherto unknown tetraborates of the alkaline earths is speculative. The metaborate or 1:1 borate occurs generally, probably on account of the tendency of the more complex ions to hydrolyse.

Borotartrates of the type $M^{II}C_4H_3O_5BO_2xH_2O$ (M^{II} = Mg, Ca, Sr, Ba) are formed[27] and their structure has been elucidated.[28]

The structure of borates in general has been very thoroughly studied recently and apart from the vast quantity of work produced by Christ and Clark *et al.* and various Russian workers, two reviews of the subject are valuable, *The Chemistry of Boron and its Compounds* by Earl L. Muetterties[231] and the 'Crystallo-chemical Classification of Borates' by G. B. Bokii and V. B. Kravchenko.[63] Alkaline-earth borates show structures of nearly every type known in borate chemistry.

More specific details of the individual borates are to be found in the following pages.

BERYLLIUM BORATES

Unlike other members of Group II and as a characteristic of its anomalous behaviour, beryllium does not readily react to form borates. The synthetic formation of a hydrated beryllium borate was not recorded until the $BeO–B_2O_3–H_2O$ system was studied hydrothermally.[29]

Anhydrous Beryllium Borates

The following anhydrous systems involving beryllium oxide and boric oxide have been studied.

System	*Characteristics*	*Ref.*
Be–B–O	Gaseous $Be(BO_2)_2$ observed	32, 33, 34
$BeO–B_2O_3$	Compound formations	35, 36, 89, 619
$Li_2O–BeO–B_2O_3$	3:1 compound formation	37–9, 5
$Na_2O–BeO–B_2O_3$	Formation possibly of a disperse phase of $Na_2O,2BeO,B_2O_3$	40
$K_2O–BeO–B_2O_3$	X-ray and ultra-violet transmission recorded	41
$Li_2O–BeO–MgO–B_2O_3$	*m*BeO,*n*B_2O_3 formation	42
$BeO–ZrO_2–B_2O_3$ $BeO–TiO_2–B_2O_3$ $BeO–Ta_2O_5–B_2O_3$ $BeO–WO_3–B_2O_3$	No glass formation and no compound formation	43

Definitive evidence for the formation of the 3:1 borate, $3BeO,B_2O_3$, was found in the study of the $Li_2O–BeO–B_2O_3$ system during an investigation into production of X-ray transparent glasses. The well-known X-ray tube window glass, Lindemann glass, is a lithium beryllium borate glass. Crystallization of the 3:1 borate is found to occur if the Li_2O content is less than the BeO content of the system.[37] The authors originally quoted the solid phase as being $2BeO,B_2O_3$. However, on re-studying the system at 800°C the compound was better characterized and found to be $3BeO,B_2O_3$.[39] More recently a study of the $BeO–B_2O_3$ system (Fig. 1) confirmed the existence of $3BeO,B_2O_3$.[35] Evidence for another unidentified crystalline phase has been given.[89] In the $BeO–Li_2O–MgO–B_2O_3$ system it was found that the presence of beryllia helps to increase the area of glass formation, but when there was a high boric oxide content and less than 15% Li_2O, crystals of the general formula *m*BeO,*n*B_2O_3 resulted.[42]

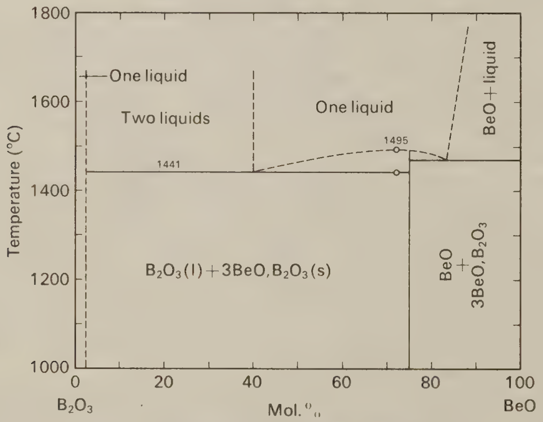


FIG. 1.—$BeO–B_2O_3$ phase diagram[35]

Sodium and potassium analogues of Lindemann glass were found to be much less stable to moisture and carbon dioxide than the lithium glass. This, together with their higher absorption of X-rays, make them less useful than Lindemann glass.[40, 41]

Some most interesting work has been carried out into the thermodynamics of the Be–B–O system at temperatures in the region of 1400 K. The vapour pressures over the system were measured isothermally and provided thermodynamic values for the vapour species and condensed phases.[32–3] Gaseous $Be(BO_2)_2$ was identified mass spectrographically in the vapour above the system.[44, 34] A study of the system by differential thermal analysis and Knudsen effusion, using a vacuum balance and mass spectrometer, showed that $3BeO,B_2O_3$ was the only condensed mixed-oxide phase.[34] The melting point of the latter was 1495 ± 5 K. The metal–anion bond strengths in gaseous $Be(BO_2)_2$ show the same relation to each other as the bond strengths in the corresponding chlorides, giving evidence for the pseudo-halide character of gaseous metaborates.[34]

Beryllium borate phosphors are reported of the composition xBeO,yB$_2$O$_3$, where $x = 1, 2, 3$ or 8 and $y = 1, 2, 3, 4$ or 5.[14,45,47] Luminescent properties of the BeO–B$_2$O$_3$ system were studied, using single crystals.[619] The orthoborate does not display luminescent emission when pure, but it is activated by Mn, Sm and Eu.

Hydrated Beryllium Borates

When beryllium salts are added to borate solution a white precipitate is formed which has been shown to be beryllium hydroxide, not a borate as one author suggested.[30] Two hydrated beryllium borate minerals are known. These are *hambergite* ($4BeO,B_2O_3,H_2O$) and *berborite* ($4BeO,B_2O_3,2H_2O$).[31] Under hydrothermal conditions, the former is formed synthetically. The trihydrate is also a solid phase of the BeO–B$_2$O$_3$–H$_2$O system, as well as $2BeO,B_2O_3,3H_2O$, BeO,B_2O_3,H_2O and $BeO,2B_2O_3,1{\cdot}2H_2O$.[29]

MAGNESIUM BORATES

Magnesium forms a wide range of both anhydrous and hydrated borates, including the double borates with calcium which occur in nature.

Anhydrous Magnesium Borates

The MgO–B$_2$O$_3$ system has been studied fully or in part by several workers.[2,48,49,50,51,254] Only three of the five established anhydrous borates are found in equilibrium according to the accepted phase diagram (Fig. 2); these are MgO,B_2O_3, $2MgO,B_2O_3$ and $3MgO,B_2O_3$. Of the other two the 1:2 compound, $MgO,2B_2O_3$ is well established[51–3] and is found in the Li$_2$O–MgO–B$_2$O$_3$ system[51]; it has also been shown to be present in the MgO–B$_2$O$_3$ system but is decomposed into $2MgO,B_2O_3$ and liquid at 1003 ± 10°C.[254] The 1:3 compound is not a stable phase in the MgO–B$_2$O$_3$ system and seems to have been a somewhat transient existence. The 2:3, 3:2, 3:4, 5:4, 7:4 compounds are mentioned in Mellor, V, 95–100, but have not been substantiated in recent years. Vaporization of B$_2$O$_3$ occurs at above 1000°C.[254] Gaseous magnesium metaborate is known.[622]

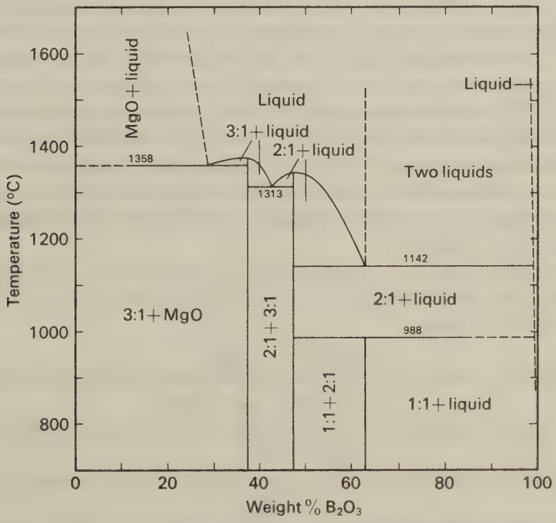


FIG. 2.—Phase diagram for the system MgO–B$_2$O$_3$.[48] (Solid phases are represented by numerals indicating their MgO:B$_2$O$_3$ ratios)

Other anhydrous ternary and quaternary systems including magnesium and boric oxides have been investigated and are listed below. Many other systems containing these oxides have also been studied with reference to glass formation.

$LiO–MgO–B_2O_3$ (ref. 5, 54, 55)
$Na_2O–MgO–B_2O_3$ (ref. 55)
$Na_2O,B_2O_3–MgO,B_2O_3$ (ref. 56)
$K_2O–MgO–B_2O_3$ (ref. 55)
$K_2O,B_2O_3–MgO,B_2O_3$ (ref. 56)
$BaO–MgO–B_2O_3$ (ref. 57)
$BaO,B_2O_3–MgO,B_2O_3$ (ref. 7)
$CaO,B_2O_3–MgO,B_2O_3$ (ref. 7)
$CdO,B_2O_3–MgO,B_2O_3$ (ref. 7)
$SrO,B_2O_3–MgO,B_2O_3$ (ref. 7)
$Li_2O–BeO–MgO–B_2O_3$ (ref. 42)
$Al_2O_3–SiO_2–MgO–B_2O_3$ (ref. 58)

A study of the formation of two liquid phases at temperatures above the liquidus when magnesium oxide is added to boric oxide has been described, together with details of surface tension measurements.[2,626] Viscosities and electrical conducitivities within the molten system $MgO–B_2O_3$ have been measured.[670] In conjunction with some general work on the synthesis of magnesium spinels the action of fusing magnesite with boric oxide has been studied.[89] The effect of boric oxide additions to polycrystalline magnesium oxide on its electrical conductivity has been investigated[93], as well as its effects on firing shrinkage, porosity, bulk density and strength at high temperatures.[623–4]

MgO,B_2O_3. This compound is formed exothermically when magnesium oxide and boric oxide are heated together in the correct ratio at 580°C.[59] It is also found as a stable phase in the $MgO–B_2O_3$ system[2,48–50] and in the $Li_2O–MgO–B_2O_3$ system.[54] It is formed together with the 3:1 compound when an excess of boric oxide is reduced with magnesium to produce boron.[60] The formation of the 1:1 compound was also detected when magnesite blocks were being sintered together with boric acid at high temperatures.[61] It is the final dehydration product of heating magnesium triborate.[660]

MgO,B_2O_3 has an incongruent melting point of 988°C[50,6] and a density of 2·48–2·49 g cm^{-3}.[59] X-Ray diffraction, microscopical and thermogravimetric examinations[6] were made of the 1:1 and 1:3 compounds; other X-ray and optical data are quoted for the three important solid phases of the $MgO–B_2O_3$ system.[62]

There is an exothermic reaction when 1–36% of magnesium oxide is fused with boric oxide at 780°C, which is stated to be due to a reaction to form the 1:3 compound.[6] It is also stated that the latter compound breaks down at 1020°C to give the 1:1 borate and boric oxide again.[6] If the 1:1 compound is heated alone it decomposes into the 2:1 compound and boric oxide, which do not recombine on cooling.[59] When the 1:1 compound reacts with water under a pressure of 12 atmospheres, *ascharite* ($2MgO,B_2O_3,H_2O$) is formed.[59]

MgO,B_2O_3 reacts with the corresponding strontium, cadmium and barium borates[7]; the resulting compounds could not be identified, but their melting relationships are summarized below.

$2MgO,B_2O_3+SrO,B_2O_3$	Two compounds melting incongruently at 988° and 960°C.
MgO,B_2O_3+CdO,B_2O_3	One compound melting incongruently at 920°C.
$2MgO,B_2O_3+CdO,B_2O_3$	One compound melting incongruently at 910°C.
MgO,B_2O_3+BaO,B_2O_3	One compound melting incongruently at 1010°C.

The same reference gives further information on eutectic temperatures and polymorphic transformations. Eutectic formation has also been studied in the systems Na_2O,-B_2O_3–MgO,B_2O_3 and K_2O,B_2O_3–MgO,B_2O_3.[56]

The resistance to hydrolysis of 1:1, 2:1 and 3:1 compounds has been studied[54], the first being the least resistant and the last the most resistant.

The structure of the 1:1 compound is not proved, but it seems likely that it is better to represent it as $(Mg(BO_2)_2)_n$ than in the monomeric form. It may have a chain structure similar to that of the analogous calcium compound.[59, 63]

$Mg(BO_2)_2$ has been identified in vapour form above melts of magnesium oxide and boric oxide.[44]

$MgO,2B_2O_3$. This compound has been synthesized during a study of the Li_2O–MgO–B_2O_3 system in which it was identified as a solid phase and characterized by X-rays.[51] More recently the compound has been obtained from the MgO–B_2O_3–H_2O system at 400°C.[53] It melts incongruently at 995°C.[625]

Patents quote the use of the 1:2 compounds as a reactant for the production of alkali-metal borohydrides[13] and tri-organo boroxines.[12] Borohydrides are obtained when the borate is treated with the appropriate alkali-metal and hydrogen at 250–310°C; the boroxines are formed by treatment with boron-organic compounds of general formula R_3B (R = alkyl, alkyl aryl, aryl) at 300 lb in^{-2}, in an inert gas. It is probable that the borates used were not true compounds but mixtures approximating to the composition indicated.

Single-crystal X-ray diffraction work recently performed using the 1:2 borate indicates its structure to be a three-dimensional B–O framework of borate groups.[64]

$MgO,3B_2O_3$. The existence of the 1:3 compound appears to be somewhat transient. It is reported to be formed by the reaction of the 1:1 compound with boric oxide at temperatures above 1020°C.[65] Its structure is reported to consist of a three-dimensional lattice including single B–O rings.[63, 66]

$2MgO,B_2O_3$. This compound is found naturally in North Korea as the mineral *suanite*; after the 3:1 borate it is the best characterized anhydrous magnesium borate found in the studies made of the MgO–B_2O_3 [6, 62, 50], Li_2O–MgO–B_2O_3 [67, 54] and Li_2O–MgO–BeO–B_2O_3 systems.[42]

The X-ray data on both the synthetic compound and *suanite* agree[69, 70]; the details have been used, together with other data[71–2, 215], to prove that it is structurally analogous to the corresponding manganese, iron and cobalt compounds.[71] The structure contains $B_2O_5^{4-}$ groups of the configuration illustrated in Fig. 3; each magnesium ion is surrounded by six oxygen atoms at the apices of a distorted octahedron, the successive octahedra being linked by the $B_2O_5^{4-}$ groups into extended sheets.[69, 71] The infra-red adsorption spectra of the crystalline 2:1 compound has been determined and is given in the range 4000–400 cm^{-1}.[73] As the acid-base characteristics of

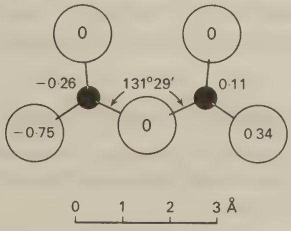


FIG. 3.—The B_2O_5 group in $Mg_2B_2O_5$.[69] (Large open circles represent oxygen and small black circles boron atoms. The heights of the atoms from the plane of the diagram (in Å) are shown)

hydrothermal solutions are of importance in explaining mineral formation, the ionization potential of *suanite* was calculated and found to be 199·3 kcal mole^{-1}.[74] The compound is reported to be paramagnetic.[75]

Boric acid and magnesium carbonate react together to form this compound at remarkably low temperatures (350–850°C); the reaction is accelerated by the addition of small quantities of sodium nitrate.

Some workers have stated that the 2:1 borate melts congruently at 1340°C[6,50] and does not combine with boric oxide to form any other borate; conversely, however, the 1:1 compound disproportionates at about 800°C to give the 2:1 compound and boric oxide.[59] In a more recent study it was found to melt incongruently at 1312°C.[625]

The incorporation of the 2:1 and 3:1 compounds in graphite by hot pressing of a mixture of graphite, magnesium oxide and boric oxide, and annealing at 850°C produces a dimensionally stable boron-containing graphite which has an expansion of less than 0·2% over a range of 800°C.[76] Another high-temperature property is its reaction with excess boron in vacuo at 880–1800°C to produce, when condensed, the polymeric $(BO)_n$.[77]

$3MgO,B_2O_3$. The best defined of all anhydrous magnesium borates is found in nature as *kotoite* (*cotoite*) and has been isolated from the same systems as the 2:1 and 1:1 borates. It is formed as orthorhombic, needle-like crystals, directly from the oxides in the right ratio by heating them in a zirconia crucible.[78] A study of the growth of the 3:1 crystals was made by adding about 4% of boric oxide to magnesium oxide at 1200–1500°C[79]; its resistance to hydration was confirmed by the same workers (cf.[5, 54]). The volatility of the 3:1 borate has been studied.[527] With traces of germanium and manganese added during its synthesis it becomes a phosphor.[92]

The incidental formation of this borate, with the 1:1 borate, during the sintering of magnesite blocks containing added boric oxide[61], and with the 2:1 borate in the periclase (magnesium oxide) linings of glass furnaces[80] has been recorded. In the latter case a mechanism for its synthesis is proposed.

Both the 3:1 and 1:1 borates are formed during the production of elemental boron from boric oxide and magnesium, when boric oxide is in excess.[60]

The 3:1 borate (or orthoborate) has a congruent melting-point of 1366°C[50, 62], the highest among values for the well characterized anhydrous magnesium borates; other workers report congruent melting at 1410°C.[625] Its structure has been investigated by means of X-ray[68,78,81] and infra-red techniques[8, 246]; the compound is isomorphous with the analogous cobalt borate ($3CoO,B_2O_3$).[78, 82] The infra-red spectra suggest a dimeric arrangement of the anions, but the X-ray work definitely indicates the existence of monomeric BO_3 triangle in a lattice in which the metal ions are six co-ordinate.[78]

One interesting chemical reaction is quoted[83] for the 3:1 compound with magnesium fluoride:

$$3MgO,B_2O_3+3MgF_2 \xrightarrow{1350^\circ} 6MgO+2BF_3.$$

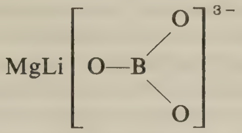
The magnesium oxide so produced is reported to be extremely inert to hydration by water. Certain intermediate addition compounds are also reported apparently related to the 3:1 borates, these being $3MgO,B_2O_3,MgF_2$; $3MgO,B_2O_3,3MgF_2$ and $3[3MgO,B_2O_3],MgF_2$.[246] The crystal structure of β–Mg_2BO_3F has been determined.[628]

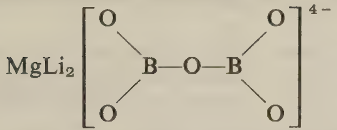
Magnesium Double Borates

Magnesium Lithium Borates. Lithium borate ($LiBO_2$) reacts with magnesium oxide to give two compounds[84], Li_2O,MgO,B_2O_3 and $Li_2O,2MgO,B_2O_3$. The former decomposes if the melt is slowly cooled,

$$2(Li_2O,MgO,B_2O_3) \rightarrow Li_2O,2MgO,B_2O_3+Li_2O,B_2O_3,$$

but if the melt is quenched it does not disproportionate in this way but retains the formula Li_2O,MgO,B_2O_3. The structures proposed by the authors of this work and by others[63] are:





Magnesium Titanium Borates. Two anhydrous salts are mentioned in the literature: $2MgO,Ti_2O_3,B_2O_3$ (formed by electrolysis at 850–900°C)[85], and $3MgO,TiO_2,B_2O_3$ (or $Mg_3Ti[B_2O_6]O_2$); the latter makes an isostructural pair with $Ca_4[Si_2O_7](F,OH)_2$ and has enabled some light to be shed on the structure of some calcium cement compounds.[86] $3MgO,TiO_2,B_2O_3$ is one end-member of the warwickite series of minerals $3(Mg,Fe)O,TiO_2B_2O_3$, with Mg > Fe. *Hulsite* occurs naturally[630] and has been synthesized.[632]

Magnesium Tin Borates. The compound MgO,SnO_2,B_2O_3 may be produced by heating a mixture of magnesium oxide, stannic oxide and boric acid (or borax) in an autoclave.[87] This compound is an analogue of CaO,SnO_2,B_2O_3, which has also been synthesized in a similar manner and is known in nature as *nordenskiöldine*. These compounds and others of the general formula MO,SnO_2,B_2O_3 have a *dolomite* structure.[10]

Magnesium Iron Borates. The magnesium end-member of the ludwigite series of minerals is $4MgO,2Fe_2O_3,B_2O_3$, for which conditions of formation have been investigated.[43, 88] The pH of hydrothermal solutions has been shown to be very important in the formation of ludwigite and associated minerals.[74] Infra-red studies of ludwigite and the iron end-member *vonsenite* have been carried out in an attempt to derive their constitutions.[90]

In a thermomagnetic study of a number of 'boroferrites' the compound $2MgO,Fe_2O_3,B_2O_3$ was produced. The magnetic susceptibilities of the compounds were studied over the range 0–1100°C; decomposition occurred above 1100°C.[91] The research was repeated more recently.[629]

Magnesium Thorium Borates. The high magnesia corner of the $MgO–ThO_2–B_2O_3$ system was studied at 1200°C, but no ternary phase was found and no solid solutions were detected.[634]

Unsynthesized minerals

The following anhydrous double magnesium borates are reported to exist but few have been synthesized:

$Al_2O_3,2MgO,B_2O_3$ (sinhalite) (ref. 631)
$6CaO,5MgO,MnO,6B_2O_3$ (kurchatovite)
$9MgO,10(Al,Fe,B)_2O_3,4SiO_2$ (sapphirine)
$(Mg,Fe^{2+},Fe^{3+}Al)_{40}(Si,B)_{18}O_{86}$ (very variable) (kornerupine)
$(Ca,Mg)_5Al_5BSi_3O_{20}$ or $Ca_2Mg_4Al_6B_2Si_4O_{26}$ (serendibite)
$[(Fe^{2+},Mg,Fe^{3+},Sn)_3B_3O_2]$ (hulsite) (refs. 630, 632)

Hydrated Magnesium Borates

Nickolaev and Chelishcheva first studied the $MgO–B_2O_3–H_2O$ system in 1940.[94, 119] They found that the system took considerable time to reach equilibrium, periods of weeks and even months were not uncommon for stable equilibrium conditions to be obtained. In 1957, details of studies made at 25, 35 and 83°C were published by d'Ans and Behrendt.[95] At the same time they also studied the $MgO–MgCl_2–B_2O_3–H_2O$ system and found that the addition of magnesium chloride to the other constituents modified the types of solid phase appreciably. Russian workers subsequently studied the formation of magnesium diborate in solutions of sodium, potassium and magnesium chlorides.[635] Rza Zade *et al.* confirmed Nikolaev's original work on the system[115] (see Figs. 4 and 5) and also investigated the above-mentioned quaternary system at

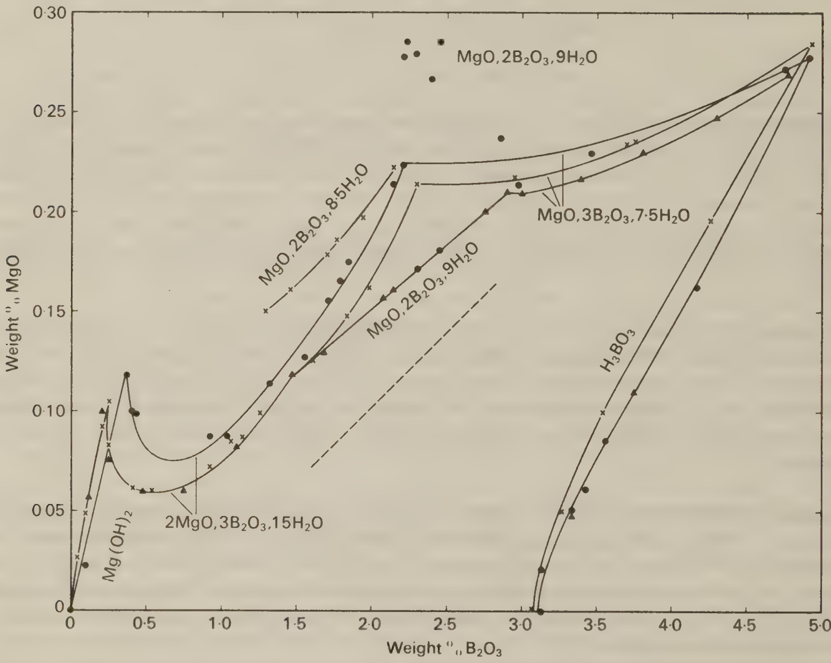


FIG. 4.—Isotherms for the system $MgO–B_2O_3–H_2O$ at 25°C; points obtained by Rza Zade et al.[115] are shown as ●, those of Nikolaev and Kurnakova as ▲, and those of d'Ans and Behrendt[95] as ×

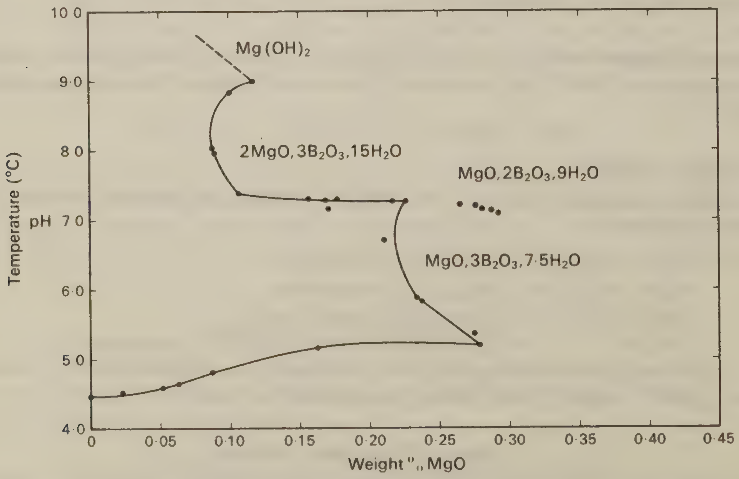


FIG. 5.—Crystallization diagram of the system $MgO–B_2O_3–H_2O$ at 25°C and its relationship to pH[95]

25[127] and 70°C.[96] Grigor'ev, in conjunction with Nikolaev and Nekrasov[53, 97] worked on the simple system at very high temperatures; at 400°C an anhydrous 1:2 borate was produced. Kesans dealt with Russian work on the hydrated magnesium borates in a general review on the formation of hydrated borates.[21] Nies and Campbell[22] have more recently reviewed the field.

Small percentages of boric oxide can be extracted from solution by means of magnesium oxide and magnesium oxychloride cements as absorbents[98–9], giving a method for the recovery of boron at high dilutions; almost certainly magnesium borates are formed.

A refractometric investigation has been carried out of the effect of addition of magnesium salts to compounds containing boron.[100] Another investigation indicated that all the known significant hydrated borates in the system Na_2O–CaO–MgO–B_2O_3–H_2O could be represented by three ternary diagrams.[101] The more complex system Na_2O–K_2O–MgO–CaO–B_2O_3–H_2O has also been studied physico-chemically.[560]

If the pH of a borax solution is held at 9 whilst magnesium chloride is added at a rate such that the temperature is not raised by more than a few degrees, a solution is formed at 27–30°C which will precipitate magnesium metaborate on heating or reducing the pH.[102]

The following systems are of interest in relation to the techniques of production of boric acid from magnesium-containing ores:

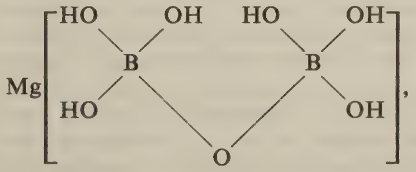
$MgSO_4$–H_3BO_3–H_2O at 25°, 55°, 65° (ref. 103)
$MgSO_4$–H_3BO_3–H_2O at 10–90° (ref. 104, 105)
$MgSO_4$–H_3BO_3–H_2O at 50° (ref. 106)
Na_2SO_4–$MgSO_4$–H_3BO_3–H_2O at 15° (ref. 107)
Na_2SO_4–$MgSO_4$–H_3BO_3–H_2O at 60° (ref. 108)

$MgO,B_2O_3,3H_2O$. This compound occurs naturally as *pinnoite*, found originally in the Stassfurt salt deposits. Until recently it was the only 1:1 borate of a Group-II metal found in nature, and it was supposed that owing to the low basicity of magnesium oxide it was capable of being formed at a lower pH than the other corresponding alkaline-earth borates, which need at least pH 11 for their formation.[21]

The original van't Hoff synthesis of this borate was confirmed[109, 21] by dissolving 0·26 mole of borax in 450 ml of warm water, adding 0·32 mole of magnesium chloride hexahydrate in 50 ml of water, and seeding the amorphous precipitate thus formed with natural pinnoite. After 7–8 days at 100°C in a closed vessel, crystals of pinnoite formed. The compound has since been isolated from the system MgO–B_2O_3–H_2O at 83°C[95] but was not found at 25 and 35°C; it was produced within a few minutes by boiling the 1:2:9 compound with boric acid solution. High surface area precipitates were formed when sodium or potassium diborates were reacted with magnesium chloride solution.[661]

This compound is also formed if the temperature is above 10°C when magnesium sulphate and potassium 1:2 borate are reacted together in water in a 1:5 molar ratio. At temperatures below 10°C, $K_2O,MgO,3B_2O_3,15H_2O$ is formed.[110]

The structure of pinnoite and the synthetic equivalent may be represented by the formula



i.e. the borate ion contains a dimer of $B(O,OH)_4$ tetrahedra. This structure was suggested by certain crystal-structure studies[111] and has recently been modified by a study of the infra-red spectrum of the isotopically labelled compound, which shows that there is only a very small coupling effect between the vibrations of the two tetrahedra.[112] In a 0·5 molar boric acid solution complex formation is considered likely, according to cryoscopic and conductimetric measurements.[113]

A study of the solubility of pinnoite in comparison with hydroboracite, inyoite and preobrazhenskite shows that at 25°C 0·65% of B_2O_3 is found in a saturated solution, and that it increases to 1·05% of B_2O_3 at 100°C. The rate of dissolution increases nearly six-fold between 25 and 95°C.[112] These data do not agree with other values, e.g. 0·1% MgO,B_2O_3 at room temperature.[95]

The compound is unstable to water. It breaks down into amorphous material, which on being heated at 150°C in a sealed tube with sodium chloride and boric acid transforms itself into ascharite (2:1:1 borate).[109, 114] It is claimed to be metastable in the MgO–B_2O_3–H_2O system and exists in conjunction with the stable phases into which it will transform, given sufficient time and favourable conditions.[115] Solubility within the system at 150°C has been studied.[636]

It is highly soluble in ammonium chloride; the solution deposits crystals containing magnesium, ammonium, chloride and borate ions.[113]

$MgO,B_2O_3,4H_2O$ and $MgO,B_2O_3,8H_2O$. Neither of these compounds has had its composition confirmed recently. The octahydrate seems to have been fairly well substantiated by four investigations (Mellor, V, 98); but the evidence for the tetrahydrate is somewhat flimsy.

$MgO,2B_2O_3,2\frac{1}{2}H_2O$. This compound is known only as the mineral *halurgite* (*galurgite*).

$MgO,2B_2O_3,4H_2O$. A recent reference quotes this compound as having the structural formula $Mg[B_4O_4(OH)_6],H_2O$ and as being a metastable phase in the MgO–B_2O_3–H_2O system.[116]

$MgO,2B_2O_3,9H_2O,8\frac{1}{2}H_2O$. A mineral corresponding to $MgO,2B_2O_3,9H_2O$ has recently been discovered in China and is called *hungchaoite*. It corresponds[117] in chemical composition and physical properties to the compound of the same formula shown to be a stable phase of the MgO–B_2O_3–H_2O system at 25°C.[119] Other workers have doubted the veracity of the formula $MgO,2B_2O_3,9H_2O$ and maintain it to be $MgO,2B_2O_3,8\frac{1}{2}H_2O$.[95] It is perhaps significant that the latter hydrate is reported to decompose after 10–15 days[95] and that the original work[119] carried out on the system, reporting the 1:2:9 compound, took many months to complete owing to the slowness in reaching equilibrium.

The 1:2:9 compound is also reported to be formed by the following reaction at 100°C[118]:

$$4H_3BO_3 + Mg + 4H_2O = MgO,2B_2O_3,9H_2O + H_2.$$

The compound is isomorphous with the corresponding manganese compound ($MnO,2B_2O_3,9H_2O$)[109] and in its habit resembles borax. Two workers[118, 119] describe the crystals as being hexagonal, but recent work on the mineral indicates that it is composed of monoclinic twin crystals.[120, 121] In the latter reference the cell parameters and space-group of the compound are also reported. Further details of the crystal structure[561, 620] and the infra-red spectrum of this compound[562] have been deduced.

Pinnoite is formed from this compound by boiling with boric acid solution.[21] There seems to be good evidence for the 1:2:9 compound, both as a mineral and as a synthetic compound, but it needs further work to determine its relationship to the $8\frac{1}{2}$-hydrate.

$MgO,3B_2O_3,5H_2O$. This compound is prepared by heating a 1:6 molar ratio of magnesium oxide and boric acid together in a closed vessel for 1–2 weeks at 100°C.[122] It may also be prepared by heating the 1:3:7½ compound in a magnesium chloride solution (saturated at 60°C) under the same conditions.[122] It is found in the $MgO-MgCl_2-B_2O_3-H_2O$ system, but hydration of the product varies with the concentrations of the constituents.[123] This compound has been shown to be identical with the recently discovered mineral *aksaite*[124], but the original report on its chemical analysis indicated a different formula.[125]

X-Ray data[122, 124] show that it may have a similar structure to pinnoite,[122] whereas other evidence[124–5] was quoted to place aksaite in the same structural order as tunnelite ($SrO,3B_2O_3,4H_2O$).[63] There is also a more recent study of the crystal structure of the compound.[420]

The crystals have a density of 1·88 g/cm^3 at 20°C.

It is stable under usual atmospheric conditions, not being readily attacked by water or carbon dioxide.[122] It is also stable up to a temperature of 230°C, at which it starts to lose its water, indicating that this is firmly bound and presumably all present as water of constitution.[122] When heated to 500°C the material becomes amorphous, and at temperatures above 700°C melts, forming the 1:1 compound and boric oxide.[122]

$MgO,3B_2O_3,6H_2O$. A study of the $MgO-MgCl_2-B_2O_3-H_2O$ system suggested that the 1:3 borate hydrates 5, 6, 7 and 7½ can be formed, depending on the concentrations of the reactants.[123] Three hitherto unknown borates, the 1:4:9, 2:3:3, and 1:3:6, were formed by crystallization from a solution of the 1:1 magnesium borate in boric acid solution. The formation and identity of these compounds was studied by conductivity and cryoscopic measurements, together with quantitative analysis of the solid phases.[126] It is a possibility that the 1:3:6 compounds and the following one have only a transient existence.

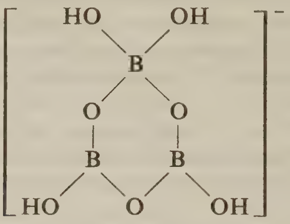
$MgO,3B_2O_3,7H_2O$. This compound is reported to be formed in the $MgO-MgCl_2-B_2O_3-H_2O$ system.[123]

$MgO,3B_2O_3,7\frac{1}{2}H_2O$. In contrast to the hexa- and hepta-hydrates of the 1:3 magnesium borates, this compound is well substantiated and is formed as one of the three stable phases in the $MgO-B_2O_3-H_2O$ system[119] at 25, 35 and 83°C.[95] It took 43 days at 25°C to obtain the crystalline material, but only about half that time if boric acid was in excess.[109] Alternatively it may be formed using the following method: 4 g of borax and 2·3 g of boric acid are dissolved in 35 ml of water, and the solution is mixed with 2·5 g of $MgSO_4,7H_2O$ dissolved in 15 ml of water. The solution remains clear for a time but starts to crystallize after 1–2 days.[21]

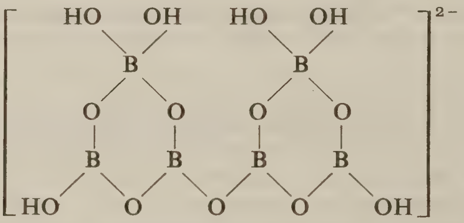
This hydrate is also to be found as a solid phase in the $MgO-MgCl_2-B_2O_3-H_2O$ system[127]; it is formed at a pH of 5·2–7·2.[115] However, if the concentration of magnesium chloride is greater than 25% the 1:3:7½ compound becomes unstable and transforms into the 1:3:5 compound at 100°C after 1–2 weeks.[95]

In 1965 a mineral whose formula corresponded to a 1:3:7½ borate was reported from two different sources and named *trigonomagneborite*[128] and *macallisterite*.[558]

X-Ray powder-diffraction patterns are given for the synthetic compound[122] and for the mineral.[128] Differential thermal analysis was used by one worker to identify macallisterite[558], and the thermal dehydration curve was studied by other investigators[122] to prove the difference between the 1:3:5 and 1:3:7½ borates. $MgO.3B_2O_3.7{\cdot}5H_2O$ dehydrates with the formation of an intermediate hydrate with 1·5 molecules of water.[662] Dehydration rates have been measured.[627] A study of the infra-red spectra of the magnesium and alkaline-earth 1:3 borate hydrates showed that it is necessary to differentiate between reversible 'hydrate states' and irreversible 'constitution hydrates' before using the infra-red data in the usual manner to define molecular structure. The compound dehydrates in two stages[95] with the loss of 3½ molecules of water initially, indicating that there are 3 molecules of water of constitution. From this evidence and X-ray data it was concluded that the formula should be represented as $Mg(B_3O_3(OH)_4)_2,3{\cdot}5H_2O$, the anion being represented by the formula



More recently however, a double-ring structure has been proposed, empirically written as $Mg_2(B_6O_7(OH)_6)_2,9H_2O$ and having a structure of the kind indicated below[563]:



The ring linkage is arbitrarily shown. Other workers have proposed the structural formula $Mg[B_6O_9(OH)_2].6{\cdot}5H_2O$.[660] Six molecules of water were lost at 140–200° and the remaining $1{\cdot}5H_2O$ at 200–450°C. Anhydrous MgB_2O_4 was the final dehydration product.

The mobility of the magnesium and alkaline-earth triborate ions in 3% boric acid was 10·25 mho/cm² and 34 mho/cm² in water, indicating that hydrolysis occurs probably to the following scheme.[23]

$$MgB_6O_{10} \leftrightharpoons Mg^{2+} + B_6O_{10}^{2-}$$
$$Mg^{2+} + B_6O_{10}^{2-} + 3H_2O \leftrightharpoons Mg^{2+} + B_4O_7^{2-} + 2H_2BO_3$$
$$Mg^{2+} + B_4O_7^{2-} + 2H_3BO_3 + 3H_2O \leftrightharpoons Mg^{2+} + 2BO_2^- + 4H_3BO_3$$
$$Mg^{2+} + 2BO_2^- + 4H_3BO_3 + 3H_2O \leftrightharpoons Mg^{2+} + 6H_3BO_3$$

$MgO,4B_2O_3,xH_2O$. This compound with $x=4$ is known as the mineral *paternoite* and has not yet been synthesized. The 1:4:9 compound, however, is not found in nature and is formed by reacting the 1:1 borate with boric acid solution.[126] Rhombic $MgB_6O_9(OH.BO_3)_2,nH_2O$ has been studied crystallographically.[621, 633] The water, $n \simeq 3{\cdot}9$ molecules, is held in a zeolite-type structure.

$MgO,5B_2O_3,4H_2O,6H.CON(CH_3)_2$. This interesting compound, with dimethylformamide incorporated into its structure, is formed with evolution of hydrogen by dissolving magnesium in a solution of boric acid in dimethylformamide. The product apparently corresponds to $Mg(B_5O_6(OH)_4)_2,6H.CON(CH_3)_2$.[130]

$2MgO,B_2O_3,H_2O$. This compound is very well known as the widely-spread mineral *ascharite* (or *szaibelyite*, which is probably a mixture of ascharite and kotoite).[595] It is also found with magnesium progressively substituted by manganese, thus defining the *sussexite* series of minerals.

It is not found as a stable phase of the MgO–B_2O_3–H_2O system at low temperatures. It has, however, been found as a solid phase in the system at 400°C.[53] The addition of magnesium chloride modifies the solid phases considerably, and if its concentration is greater than 25% the 2:1:1 compound is formed at 83°C.[95] The hydrothermal treatment of the 1:3:5 compound at a pressure of 12 atmospheres produces a hydrated 2:1 borate which is possibly ascharite.[122] Pinnoite and kaliborite[131] hydrolyse with water to give an amorphous material which on heating with sodium chloride and boric acid at 150°C in a sealed tube gives crystalline $2MgO,B_2O_3,H_2O$.[21, 114] Hydroboracite also reacts very slowly to give ascharite.[132] Recently the conditions for formation of ascharite[43, 74] and the endogenetic magnesium iron borates have been postulated.[43]

Ascharite is the most dense (ρ 2·62) of the simple magnesium borate ores; it is also the least water-soluble of all calcium and magnesium borates.[133] An equilibrium solution at 25°C contains only 0·13% of B_2O_3 and its linear rate of dissolution is less than one hundredth of that of colemanite.[112] Elsewhere the solubility of ascharite is quoted at 25°C as 0·0085% B_2O_3 equivalent.[134]

Much interest in ascharite has been shown in recent years and many studies relating to its crystal structure and its optical properties have been made.[135–6] It has orthorhombic symmetry which is so characteristic that extremely small quantities have been identified by means of the electron microscope.[137] X-Ray studies have been made of ascharite and the derived sussexite minerals[137–9], and infra-red spectra have also been used in determining the structure of the anion.[139, 140] The evidence to date indicates the possibility of the structure $Mg_2(B_2O_4OH)OH$.[63] Thermal analytical work on ascharite, in conjunction with other borates, has been performed.[141] Synthetic $2MgO,B_2O_3,H_2O$ was found to dehydrate to $2MgO,B_2O_3$ at 365°C.[662]

The solubility of ascharite in water as well as in saturated solutions of calcium sulphate and sodium chloride has been studied at 25°C[46], and the inhibiting effect of the presence of liquors containing magnesium sulphate and boric acid on the decomposition of ascharite by sulphuric acid is described.[142] It is interesting to note that even though ascharite is quite insoluble in water it is readily dissolved by solutions containing carbon dioxide and calcium sulphate, to give magnesium sulphate and boric acid.[133]

$2MgO,B_2O_3,2\frac{1}{2}H_2O(3H_2O)$. The existence of the $2\frac{1}{2}$ hydrate has been shown by two workers.[95, 127] In a metastable form it is found as a solid phase in the MgO–$MgCl_2$–B_2O_3–H_2O system. The compound has been studied by optical, thermogravimetric and X-ray techniques[32] and one author reports it to have a similar X-ray pattern to ascharite.[95] The 2:1:3 compound is also reported by d'Ans and Behrendt[95] to be formed by refluxing inderite (2:3:15) in a 50% solution of magnesium chloride hexahydrate for 4 days. The distinction between this compound and the $2\frac{1}{2}$ hydrate is difficult; it would be necessary to compare closely X-ray patterns and other crystal properties before deciding that they are definite entities.

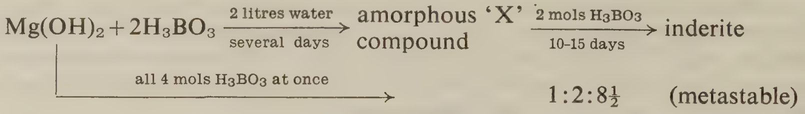
$2MgO,3B_2O_3,xH_2O$. Hydrates with $x = 3$, 5, 13, 15 and 17 have been reported.

The 3, 5 and 17 hydrates are referred to only once each in the literature. The former is reported to be produced by reacting the 1:1 borate with a dilute solution of boric acid[126]; the latter was formed whilst investigating the extraction of boron from solutions by precipitation with magnesium salts.[143] This compound is reported as having a density of 1·61 and the following refractive indices: $Ng = 1{\cdot}502$ and $Np = 1{\cdot}486$. It loses water at 65–70°C to give the 2:3:5 compound.[143]

The 2:3:13 compound as a mineral was for some years (1941–60) given the name of *kurnakovite* (triclinic) and was originally found in conjunction with the 2:3:15 compound known as *inderite* (monoclinic) in Lake Inder.

In 1960 it was suggested that both kurnakovite and inderite had the same formula[144], and in 1963 this was confirmed[145], the formulation being 2:3:15. Further confusion arose when a new mineral *lesserite* was discovered at Boron, California, which later was proved to be inderite. It seemed then that both kurnakovite and inderite have the same formula but are distinct minerals. In 1965, however, the situation became less clear by the reporting of the existence of the 2:3:13 compound in conjunction with the 2:3:15 borate in the MgO–$MgCl_2$–B_2O_3–H_2O system at 25°C.[127]

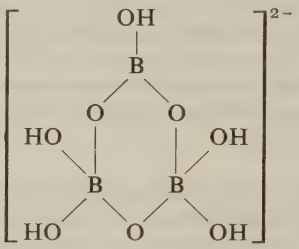
The 2:3:15 compound in the form of kurnakovite has been synthesized by crystallization from a saturated solution of kaliborite.[146] On the other hand the compound in the crystal form of inderite has been found in the $MgO–B_2O_3–H_2O$ system at 25°C after 97 days, and the $K_2O–MgO–B_2O_3–H_2O$ system at 25°C after only 40 days.[147] It was also found to occur in the $MgO–B_2O_3–H_2O$ system at 35°C but not at 83°C[95] and may, in addition, be crystallized from a solution of borax at 35°C by the addition of magnesium sulphate.[148] The conditions of more rapid formation from magnesium hydroxide and boric acid are as follows.[95]



Inderite has been shown to crystallize at pH 7·2–9·0 in the $MgO–B_2O_3–H_2O$ system at 25°C[115] and is also to be found as one of the ten solid phases in the $MgO–MgCl_2–B_2O_3–H_2O$ system.[127] A compound close to the inderite composition was obtained from mixing equal volumes of 0·7M $MgCl_2$ and potassium tetraborate solutions.[661] Both potassium and ammonium magnesium borates ($M_2O,MgO,3B_2O_3,xH_2O$) hydrolyse with water over a period of days to give inderite.[21] Inderite is a solid phase of the $NaCl–KCl–MgCl_2–KOH–B_2O_3–H_2O$ system at 25°C.[564]

Inderite has a specific gravity of 1·78.[94, 148] Its crystal structure has been studied, especially to compare it with kurnakovite.[119, 144, 149]

The anion in the inderite structure is probably a ring of the form



giving an overall formula of $Mg[B_3O_3(OH)_5],5H_2O$. It has been deduced from the ^{11}B nuclear magnetic resonance spectrum that two of the borons are tetrahedrally co-ordinated and the other triangularly co-ordinated, thus supporting the above formula. Other evidence also implies this formula.[145, 150] The structure of kurnakovite has recently been studied again[151, 152] and could be represented by a formula corresponding to $Mg\{[B_3O_3(OH)_5]4H_2O\}H_2O$ with one molecule of water differing from the other four.[565] Heating curves of synthetic inderite show that there is an endothermic heat effect due to loss of water up to 450°C and that at 600–700°C it changes to an exothermic effect connected with its change of solid state. The identity of synthetic and natural inderite was also proved by the characteristic heating curve[148] and the refractive indices.[119]

Inderite is decomposed by refluxing with a 50% solution of magnesium chlorile hexahydrate, when the 2:1:3 borate is formed.[95]

During a study of the thermal decomposition of magnesium borates at various pressures, the 2:3:15 compound was observed to dehydrate in four stages.[662] Pinnoite and 1:2:9 were formed at 170–200°C; the 1:2:9 compound dehydrated to $MgO,2B_2O_3$ at 400–545°C, but through two intermediate borates: 1:3:5 (110–140°C) and 1:2:3 (270–460°C).

$3MgO,B_2O_3,11H_2O$. One reference to this compound is to be found in some recent work on the $MgO–MgCl_2–B_2O_3–H_2O$ system at 25°C. The crystals isolated were biaxial and positive with $N_\gamma = 1·506$ and $N_\alpha = 1·488$. Heating curve data are quoted.[127]

$3MgO,5B_2O_3,4\frac{1}{2}H_2O$. This is known only as the mineral *prebrazenskite* and has not yet been synthesized; its formula has alternatively been quoted as 4:7:6[112, 153], and 3:5:5.[154]

$6MgO,7B_2O_3,H_2O$. This borate has recently been reported in some work on the $MgO–B_2O_3–H_2O$ system at 400°C.[53]

$9MgO,B_2O_3,2H_2O$. This is only known as the mineral *wightmanite*. It has not been synthesized.

Hydrated Magnesium Double Borates

Magnesium Ammonium Borates. Only one magnesium ammonium double salt has been reported. If a magnesium sulphate solution (2·5 g of $MgSO_4$ in 30 ml of water) is added to a solution of 12·3 g of boric acid in 150 ml of water, containing 0·1 mole of ammonia, the solution starts to throw out crystals of $(NH_4)_2O,MgO,3B_2O_3,xH_2O$ after about 24 hours. Crystallization can be accelerated by scratching the beaker, when it occurs after only a few hours.[155] If the product is washed with alcohol and then ether, or dried at above 20°C, the product is heptahydrated. Alternatively by drying over phosphorus pentoxide at 20°C the 15 hydrate is obtained. If the heptahydrate is heated at a temperature between 25 and 70°C, water is driven off until only the equivalent of $4H_2O$ is left. Above 100°C ammonia is evolved, and at 130°C all the ammonia is lost, as well as 1 molecule of water. Above 130°C the final 3 molecules of water are lost. The product hydrolyses slowly to give large prisms of inderite ($2MgO,3B_2O_3,15H_2O$).[21]

Magnesium Sodium Borates. Some years ago fairly well-substantiated work (Mellor, V, 99) was done on the production of $Na_2O,2MgO,5B_2O_3,30H_2O$. In addition the mineral *rivadavite*, $3Na_2O,MgO,12B_2O_3,22H_2O$[156], has recently been discovered. Apart from this evidence, however, the only modern work on this subject is negative.[21] Unsuccessful attempts have been made to produce a sodium analogue of the ammonium magnesium borate referred to above. The lack of success is thought to be due either to the impossibility of getting the right pH conditions or to the hydration of the sodium ion.[21]

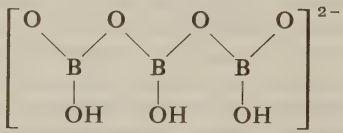
Magnesium Potassium Borates. Two hydrates of the form $K_2O,MgO,3B_2O_3,xH_2O$ have been synthesized. The 15-hydrate is the best characterized and may be prepared by prolonged agitation of a mixture of 2·5 g of $MgSO_4,7H_2O$ with 15 g of $K_2B_4O_7,4H_2O$ in 100 ml of water at 5–10°C.[110] The optimum pH for the formation of this compound is 9·0–11·0.[157] Further work on the formation of $K_2O,MgO,3B_2O_3,xH_2O$ from the reaction of magnesium chloride and $K_2B_4O_7$ is reported.[594] A lower hydrate, $K_2O,MgO,3B_2O_3,9H_2O$, has also been found.[143]

Other reported borates of this kind are the minerals *kaliborite*, $4MgO,K_2O,11B_2O_3,18H_2O$, and *heintzite*, $4MgO,K_2O,11B_2O_3,14H_2O$. The former has been synthesized (Mellor, V, 99). Kaliborite hydrolyses to give an amorphous compound which, if heated at 150°C in a sealed tube with sodium chloride, forms ascharite ($2MgO,B_2O_3,H_2O$). A study of the effect of hydrolysis and the reaction with solutions of gypsum has been carried out with a view to providing information on the autotransformation of boron minerals.[46] With a solution of calcium sulphate at 25°C kaliborite is transformed into hydroboracite ($CaO,MgO,3B_2O_3,6H_2O$) and inyoite ($2CaO,3B_2O_3,13H_2O$).[114, 132]

$K_2O,MgO,3B_2O_3,15H_2O$ loses 10 molecules of water between 30 and 60°C and a further 2 between 60 and 100°C. The final 3 molecules are driven off between 100 and 350°C, and at 700°C the product sinters. The compound hydrolyses in much the same way as the ammonium analogue, producing inderite.[110]

Magnesium Calcium Borates. Two compounds $CaO,MgO,3B_2O_3,6H_2O$, *hydroboracite*, and $CaO,MgO,3B_2O_3,11H_2O$, *inderborite*, have been synthesized. The former is produced by heating to boiling point a mixture of borax and calcium and magnesium chlorides in water, decanting, allowing the supersaturated liquid to stand under reflux at 50°C, and seeding with hydroboracite.[158] Later workers synthesized it from boric acid, lime, water and magnesium chloride, and considered thermograms and infra-red absorption spectra of the product.[647] Inderborite is formed by heating borax and the respective hydroxides together under thermostatic control for 3 months.[159] Kaliborite ($K_2O,4MgO,11B_2O_3,18H_2O$) reacts with a solution of sodium chloride and gypsum ($CaSO_4,2H_2O$) to form hydroboracite, as well as various other products.[114]

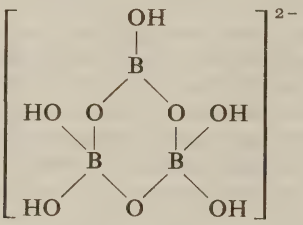
The structure of hydroboracite is quoted as $MgCa[B_3O_4(OH)_3]_2,3H_2O$[63], probably involving an anion of the structure:



(ref. 160)

A study of the dehydration of hydroboracite by differential thermal analysis[161] indicates that only 2 molecules of water are lost up to about 220°C, where there is a sharp inflection of the curve, implying a formula $CaMg[B_6O_7(OH)_8],2H_2O$. Differential thermal analysis of hydroboracite and inderite, as well as of other related borate minerals, has also been carried out.[141]

The structure of inderborite differs from that of hydroboracite in the constitution of its anion, which is reported to have a ring structure[63, 554]:



This gives the formula $CaMg[B_3O_3(OH)_5]_2,6H_2O$.

Two reports of the cell parameters of inderborite differ to some extent[162, 163], but a further paper[164] confirms the second reference.

The solubility properties of hydroboracite have been extensively investigated, owing to its use as one of the principal borate-producing minerals in the U.S.S.R. The leaching of hydroboracite with water eventually yields ascharite. It has been observed that the order of leaching is $B_2O_3 > Ca > Mg$.[132] Its solubility in saturated solutions of gypsum and sodium chloride varied little from that in water (0·23–0·26% B_2O_3 at 25°C).[46] The solubility in water is recorded as 0·08% B_2O_3 at 25°C by another worker.[134] The rate of dissolution in water was investigated at 25, 50, 75 and 95°C; it more than doubled over the extremes of this range.[112] The solubility and rate of dissolution of hydroboracite in solutions of hydrochloric acid of different concentrations showed that the rate decreased as the acid concentration decreased but in solutions with acid concentrations greater than 20% the rate remained steady. The decrease was related to the formation of a film of boric acid over the surface of the compound.[165] Similar investigations were carried out using nitric acid[164] and sulphuric acid.[166] Details of a more extensive investigation concerning temperature coefficients of dissolution rates and activation energies of dissolution of hydroboracite in hydrochloric acid solutions ranging from 2·5–30 wt.-% have been published.[167] The latter workers utilized the formula

$$V = (\tfrac{1}{2}\rho_s^{2/3}/t)(g_0^{1/3} - g^{1/3}) \text{ g cm}^{-2} \text{ sec}^{-1}$$

where V = rate of solution;
ρ_s = density of crystals;
g_0 and g = weight in g of crystals before and after experiment;
t = time in seconds.

The rates of solution with all these acids were much the same. However, it was postulated[166] that a film of calcium sulphate was the factor limiting the rate of solution at higher concentrations of sulphuric acid, not boric acid. Finally it has been shown that the presence of magnesium sulphate and boric acid, in solution during the reaction of hydroboracite with sulphuric acid, has no effect in slowing down the reaction, whereas a distinct retardation was found in the case of ascharite.[168]

Other unsynthesized magnesium borate minerals containing calcium and magnesium

Kurchatovite, $CaO,5MgO,MnO,6B_2O_3$;
Roweite, $(Mn,Mg,Zn)O,CaO,B_2O_3,H_2O$.

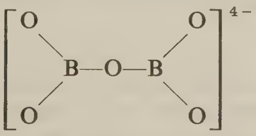
Magnesium Borates Containing Other Anions

Phosphate

$2MgO,Mg_3(PO_4)_2,B_2O_3,8H_2O$. This compound is found in nature as the mineral *leunebergite* but has also been synthesized by two methods.

(a) An identical compound to leunebergite (according to the X-ray powder diagram) is formed by mixing 1·0 g of magnesium oxide together with 8·1 g of $MgHPO_4,3H_2O$ and 9·2 g of boric acid in 200 ml of water, and keeping the mixture at room temperature for some weeks, or at boiling point for a few days.[169]
(b) The second method employs the slow reaction between boric acid, magnesium chloride or sulphate, and apatite (calcium phosphate fluoride).[170]

The structure of this compound has been quoted to be $Mg_5[B_2O_5](PO_4)_2,8H_2O$, where the borate anion is probably of the form[63, 171]:



The system $MgO–B_2O_3–P_2O_5–H_2O$ was studied at 90°C.[637] $2MgO,B_2O_3,P_2O_5,7{\cdot}5H_2O$ was observed as a solid phase.

Sulphates

$Mg[B(SO_4)_2]_2$, etc. This compound is not a true borate as it has properties which relate it more to the product of the reaction between boric oxide and concentrated sulphuric acid. It is formed by reacting magnesium sulphate ($MgSO_4$) with boric acid and sulphur trioxide[11]:

$$MgSO_4 + 2H_3BO_3 + 6SO_3 = Mg[B(SO_4)_2]_2 + 3H_2SO_4$$

Analogous compounds are also formed in which the metal ion is Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} or Pb^{2+}.

The compounds, except for those of nickel and cobalt, are colourless and very hygroscopic. They all seem to have similar lattice structures and are probably ionic with high-polymer anions.[11]

There is also a mineral *sulphoborite*, $2MgO,MgSO_4,B_2O_3,5H_2O$, which has not yet been synthesized, but which can be classified as a borate.

Chloride; Boracites

The best-known compound that comes under this heading is $5MgO,7B_2O_3,MgCl_2$ which is found as the mineral *boracite*. It is comparatively rarely, however, that the mineral contains only magnesium; it is better known in forms containing iron and/or manganese substituting for the magnesium, e.g. *ericaite*. Boracites have been synthesized in which the magnesium has been replaced by nickel, zinc, cadmium, lead, barium, etc.[172, 230], and in which the chlorine has been replaced by bromine and iodine giving bromo- and iodo-boracites of magnesium, iron (Fe^{2+}) and manganese (Mn^{2+}).[173] A variety of boracites can be made by varying the starting materials and a recent patent describes an interesting method whereby the metal chloride, the appropriate oxide and boric oxide are mixed with a carrier H_2O,HX ($X=$halogen), oxygen or a halogen, which is chosen such that during the heating of the mixture in a closed vessel at 300°C, the boric oxide remains in the liquid phase. Crystals of the required boracite are formed via the vapour phase and crystallize on the surface of the container.[45]

It is also possible to produce boracite as a solid phase from the aqueous system $MgO–MgCl_2–B_2O_3–H_2O$.[95]

Ferroelectric properties of boracite were predicted from theoretical considerations[174] and studied experimentally, together with elastic and piezoelectric behaviour.[172, 175] The dielectric properties of boracite have also been investigated.[172, 176]

X-Ray studies of single crystals of the two crystalline modifications of boracite (α and β) show that the structures contain both BO_4 tetrahedra and BO_3O pyramids[177] and on this evidence, in a classification of borate structures[63], boracite is placed in the 'three-dimensional lattice' type of non-ring borates, i.e. $Mg_3(B_7O_{13})Cl$.

The various crystal structure parameters, etc., for the bromo- and iodo-boracites of magnesium, Fe^{2+}, Mn^{2+} are compared with those for corresponding chloroboracites.[173]

Silicates

Boron Phlogopite $KMg_3BSi_3O_{10}(OH)_2$. This mineral has been synthesized[178] by heating potassium silicate ($K_2O,6SiO_2$), magnesium oxide and boric acid together in a sealed gold tube under 2000 bars pressure at 250–300°C, the reactant proportions being such that the ratio K:Mg:B:Si = 1:3:1:3. The optical properties were determined.

Borotartrates

A number of borotartrates of the form $MC_4H_3O_5BO_2,xH_2O$ have been synthesized, where M = Mg, Ca, Sr, Ba; in the case of magnesium compound $x=7$.[27]

Unsynthesized Magnesium Borate Minerals Containing Other Anions

FLUORIDE: *Fluoborite*, $3MgO,B_2O_3,3MgF_2$ or $Mg_3(BO_3)(F,OH)_3$
CARBONATE: *Borocarite*, $4CaO,MgO,2B_2O_3,2CO_2,3H_2O$
Carboborite, $MgO,2CaO,B_2O_3,CO_2 10H_2O$
CARBONATE CHLORIDE: *Sakhaite*, $23CaO,8MgO,7B_2O_3,8CO_2,CaCl_2 8H_2O$
SILICATE: *Tourmaline.*

CALCIUM BORATES

Anhydrous Calcium Borates

The system $CaO–B_2O_3$ was studied thoroughly by Carlson[179], confirming previous work that there are four distinct solid phases, 1:2, 1:1, 2:1 and 3:1. Apart from the unsynthesized mineral, *calciborite* ($CaO,4B_2O_3$) the only other anhydrous calcium borates are the 2:3 (?), 4:7 and 5:4 borates, which are reported to have been formed at elevated temperatures from aqueous solutions.[180] In a study of the system in which calcium carbonate and boric acid were together fired at 50°C below that at which a glassy phase was formed, and held at this temperature until solid-state equilibrium was obtained, $CaO,2B_2O_3$, $2CaO,B_2O_3$, CaO,B_2O_3 and $3CaO,B_2O_3$ were identified.[673]

Above about 77 wt.-% B_2O_3 the phase diagram[179] (Fig. 6) shows an area in which two liquid phases are in equilibrium; these can be reduced to one phase by the addition of 3 mol.-% of potassium oxide. The viscosity and electrical resistivity of the liquid treated in this way increase rapidly over the temperature range 600–800°C but become constant or slightly decrease over the range 1000–1100°C.[3, 181] Details are also given of other additions which have this homogenizing action on the liquid phases.[2] The

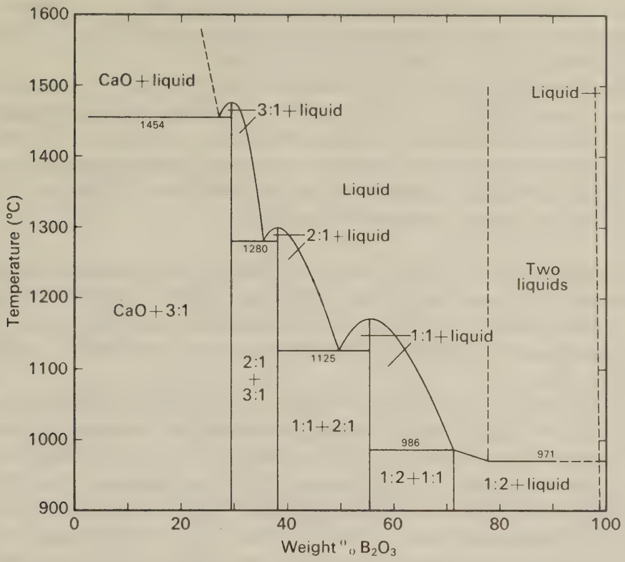


FIG. 6.—Phase diagram for the system $CaO–B_2O_3$[197] (solid phases are represented by numerals indicating their $CaO:B_2O_3$ ratios)

surface tensions in the two-liquid region are the same as that of boric oxide, and outside the region the surface tension increases as the calcium oxide content increases.[1]

Activities deduced from the liquidus curves of the $CaO–B_2O_3$ system[179] and high-temperature heat contents[182] are consistent with the presence of simple BO_3^{3-}, and $(BO_2)_3^{3-}$ ions.[183] Values of the thermodynamic quantities ΔS, ΔF[184] and ΔH[6, 185] have been determined for the four borates represented in the $CaO–B_2O_3$ system.[186] The heats of solutions of calcium borate, as well as of other alkaline-earth borates and lead borates in 2N nitric acid were measured for glassy and devitrified modifications. Tabulations of heats of fusion, entropies of fusion and entropy changes versus temperature for the borates are also available.[6] The heats of solution of anhydrous calcium borates in N hydrochloric acid have also been determined, and an expression derived, $\Delta H = -3280 - 14{\cdot}60C$, where C = g of boric oxide dissolved in 1845·5 g of N hydrochloric acid.[185] The hygroscopicity of the various borates is greatly increased by the presence of an excess of calcium oxide or boric oxide.[179]

Calcium borates activated with various metals such as lead, thallium, molybdenum, tin, bismuth and the rare earths have been the basis of a large amount of work on luminophors.

Many systems containing calcium oxide and boric oxide to which other oxides have been added have of course been studied in the glass technology field. Studies of a few of these systems, listed below, have afforded evidence of well-defined crystalline mixed calcium borates:

$Na_2O–CaO–B_2O_3$ (ref. 187)
$CaSO_4–Na_2O,2B_2O_3$ (ref. 188)
$NaCaBO_3–Na_2CO_3$ (ref. 189)
$CaO–As_2O_5–B_2O_3$ (ref. 129)
$CaO–P_2O_5–B_2O_3$ (ref. 190, 557)
$Cd(BO_2)_2–Ca(BO_2)_2$ (ref. 7)
$Sr(BO_2)_2–Ca(BO_2)_2$ (ref. 7)
$Ba(BO_2)_2–Ca(BO_2)_2$ (ref. 7)
$K_2O,B_2O_3–Ca(BO_2)_2$ (ref. 56)
$Na_2O,B_2O_3–Ca(BO_2)_2$ (ref. 56)

Theoretical temperature-composition phase diagrams were deduced from free energy-composition curves for the system $2CaO,B_2O_3$–CaO,SiO_2.[191] The activities in calcium borosilicate melts[192] have been determined.

CaO–MgO–Al_2O_3–B_2O_3 slags have been used as a medium for titanium-ion reduction reactions. Polarization of Cu–Ti, Fe–P–Ti and tungsten electrodes during the deposition of titanium was caused by the diffusion of the ions in the melt.[193]

Evidence for the occurrence of linear or laminate polyborate ions in CaO–B_2O_3 melts is given by increased conductivity in the direction of flow of the liquid and decreased conductivity when measured transversely.[194]

CaO,B_2O_3. Investigations of the CaO–B_2O_3 system have shown that the 1:1 borate or metaborate crystallizes in long, flat plates melting at 1154 ± 5°C.[179] Among other compounds a high-pressure polymorph of CaO,B_2O_3 has also been prepared by hydrothermal treatment of $Ca(OH)_2$–H_3BO_3 mixtures at 200–400°C. X-Ray data are given[195] (see Fig. 22).

Crystals of the normal compound belong to the orthorhombic system with four molecules to the unit cell.[196] X-Ray techniques show the structure to consist of BO_3 groups which join to form endless chains parallel to the *c*-axis.[197] Refinements of this original work did not alter this conclusion, but gave evidence that the three B–O bonds in the BO_3 triangle are of different lengths, 1·326, 1·385 and 1·401 Å, with the short bond to the unshared oxygen atom. The Ca–O bonds range from 2·347 to 2·727 Å.[198] The density calculated from the above data is 2·70 compared with the experimental value of 2·65. The structure of polycrystalline calcium metaborate has also been studied using a ^{11}B n.m.r. technique.[199] The crystal structures of calciborite and of four synthesized polymorphs have been determined.[654]

Study of the activities in the 1:1 or metaborate melt suggest the formation of the hexagonal ring $[(BO)_3O_3]^{3-}$ ion.[183]

Various thermodynamic properties of the compound are quoted:

$$S_{298\cdot16} = 2{\cdot}6 \pm 0{\cdot}3 \text{ cal/deg/mole (ref. 184)}$$
$$F_{298\cdot16} = -30{,}200 \pm 90 \text{ cal/mole (ref. 184)}$$
$$\Delta H_f \text{ (from oxides) (at 298·16 K)} = -29{,}420 \pm 20 \text{ cal/mole}$$
$$\Delta H_f \text{ (from elements) (at 298·16 K)} = -524{,}000 \text{ cal/mole (ref. 185)}$$
$$S = 25{\cdot}1 \pm 0{\cdot}2 \text{ cal/deg/mole (ref. 184)}$$

The heat of solution in N hydrochloric acid at 298·16 K is −20·259 ± 8 cal/mole.[185]

The electrical conductivity of the metaborate, with a slight excess of boric oxide, varies inversely with temperature. This effect is especially noticeable at low temperatures. The mechanism of conductivity is assumed to be electronic.[200]

The compound has been tested as a cyclotron target for the production of radioactive calcium. It is only 27% as efficient as metallic calcium, but allows stable operation of the cyclotron and radiation stability.[201]

A number of binary systems in which the 1:1 borate is one component and another anhydrous metaborate is the other have been studied; results are summarized in Table I.

The fluorescent properties of the metaborates activated with various metals have been studied.[14]

$CaO,2B_2O_3$. The 1:2 borate has the lowest melting point (986° ± 5°C) of the four calcium borates found in the anhydrous system CaO–B_2O_3.[179]

The thermodynamic properties of this compound have been studied and some are found in Table II.[182, 184, 185]

On the basis of some early work[179] the structure is considered isomorphous with the corresponding lithium, sodium, potassium, cobalt, strontium and lead tetraborates, in the order of three-dimensional lattice borates with double rings.[63]

Apart from its synthesis from its component oxides[179] the compound also crystallizes from the system:

$$CaSO_4 + Na_2O,2B_2O_3 \rightleftharpoons CaO,2B_2O_3 + Na_2SO_4$$

Table I.—Systems related to CaO,B_2O_3

System	Ref. no.	Mol.-% $Ca(BO_2)_2$	M.p., °C	Eutectic temp., °C	Transition temp., °C	Compound
Na_2O–B_2O_3–CaO,B_2O_3	56	50·5	—	—	89	corres. to formation of incong. compound $2NaBO_2$,-$Ca(BO_2)_2$
		28·5	—	855	—	—
K_2O,B_2O_3–CaO,B_2O_3	56	32·2	—	858	—	—
CdO,B_2O_3–CaO,B_2O_3	7	18·5	860			cong. compound
		25		836	—	—
		35·5	868	—	—	incong. compound
		45	950	—	—	cong. compound
		75	—	—	998 poly morphic	—
SrO,B_2O_3–CaO,B_2O_3	7	Continuous series of solid solutions, m.p. min, at 1062°C				
BaO,B_2O_3–CaO,B_2O_3	7	22·5	1056			cong. compound
		42	1060			incong. compound
		53·5	1080			—
		67	1074			—

Double salts of the following composition also crystallize from this system: $CaSO_4$,-CaB_4O_7; $Na_2B_4O_7,2CaB_4O_7$; $Na_2B_4O_7,2CaSO_4$. The stable diagonal $CaSO_4$–$Na_2B_4O_7$ divides the system into two triangles which differ sharply in their properties. The melts of the triangle $CaSO_4$–Na_2SO_4–$Na_2B_4O_7$ are easily crystallized and also show a great tendency to separation into layers. The melts in the triangle $CaSO_4$–CaB_4O_7–$Na_2B_4O_7$ tend to form glasses.[188]

The addition of the 1:2 borate to thoria during hot pressing at 1650°C decreases the porosity of the sintered thoria.[202]

$2CaO,B_2O_3$. This compound was produced in phase equilibrium studies[179] as crystals of irregular grain-size, m.p. 1298 ± 5°C. The synthetic compound $2CaO$,-B_2O_3,H_2O and the analogous mineral *sibirskite* completely dehydrate at 400°C to give the anhydrous compound. X-Ray data for the 2:1 compound formed in this way are recorded.[203] The synthesis and further X-ray data for $2CaO,B_2O_3$ are discussed in some later work.[204, 673]

Some thermodynamic properties are given in Table II.[182, 184, 185]

On the basis of somewhat slender evidence[179] the structure has been placed in the category of insular borates of non-ring structure containing dimers of $B(OH,O)_3$ triangles and $B(O,OH)_4$ tetrahedra.[63]

Theoretical temperature-composition phase diagrams have been deduced from free energy-composition curves, assuming ideal solutions, for the system $2CaO,B_2O_3$–CaO,SiO_2.[191]

$2CaO,3B_2O_3$. The isobaric potential of this compound has been found in the CaO–B_2O_3 system, which seems to indicate that it should be more stable than the 1:2 borate in the presence of boric oxide.[153] Reference to earlier work gives details of its formation (Mellor, V, 90). The crystal structure is framework-type and is characterized by $[B_6O_{11}]^{4-}$ polyanions, formed from four successively linked BO_4 tetrahedra with $2BO_3$ triangles closing them.[672]

$3CaO,B_2O_3$. The orthoborate crystallizes from the anhydrous CaO–B_2O_3 system as transparent prismatic crystals with a melting point of 1479 ± 5°C.[179] It may also be formed by heating its constituent oxides at 365°C for 5 hours in the presence of saturated steam.[203] The compound also forms in furnace linings in which magnesite blocks are bonded together with boric acid, if too much of the latter is added.[61] A further synthesis is also on record.[204]

Two studies of the infra-red spectra of the orthoborate ion in calcium orthoborate have been carried out.[8, 73] The results of the former work were consistent with a dimeric arrangement of ions, but it was not possible to deduce the spatial relationships of the BO_3^{3-} ion. X-Ray data are also on record[203, 204], including a determination on single crystals grown from the melt.[652, 657] The structure is classified in the order of insular non-ring borates with independent polyions[63], which is inconsistent with a dimeric arrangement deduced by other authors.[8] The BO_3 group has been stated to be non-planar, and the Ca atom to be surrounded by eight nearest O atoms forming a distorted square-antiprism.[657]

Certain thermodynamic data are given in Table II.[182, 184, 185] In the aluminothermic production of ferroboron the slags contain the 3:1 borate, which may exchange its calcium for aluminium.[559]

Study of the system $3CaO,B_2O_3$–$2CaO,SiO_2$ has resulted in the formation of two crystalline compounds of the formula $11CaO,4SiO_2,B_2O_3$, one a high-temperature form and the other a low-temperature dimorph. Lattice dimensions are given.[566]

Other Anhydrous Borates

Three other binary borates have been described recently. The 1:4 borate is only known as the mineral *calciborate* on which some data have been gathered.[206] Hydrothermal reaction of the system CaO–B_2O_3–H_2O at 200–350°C gives rise to a reported

Point	CaO	B_2O_3	SiO_2	Temp.
1	54·6	1·5	43·9	1436
2	59·2	16·0	24·8	1118
3	59·4	16·6	24·0	1128
4	66·2	14·1	19·7	1266
5	67·7	13·3	19·0	1400
6	69·2	12·6	18·2	1398

Point	CaO	B_2O_3	SiO_2	Temp.
7	69·7	16·2	14·1	1400
8	70·0	23·2	6·8	1404
9	69·4	22·8	7·8	1415
10	55·4	20·4	24·2	1150
11	45·0	31·7	23·3	1017
12	38·3	31·5	30·2	977

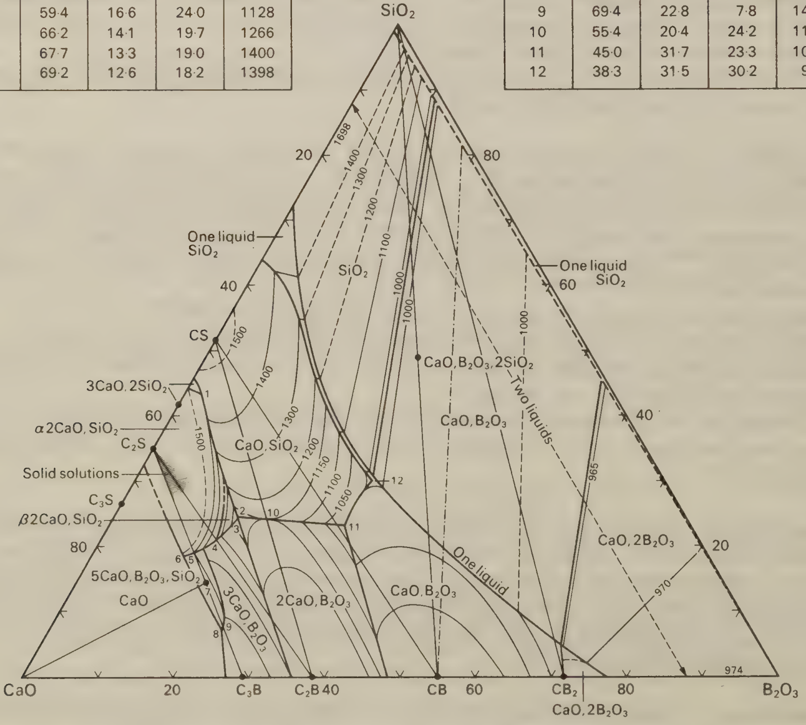


FIG. 7.—The system CaO–B_2O_3–SiO_2[209]

$4CaO,7B_2O_3$ compound.[180] At 125–340°C the hydrothermal reaction of borax and gypsum gives a solid phase corresponding to $5CaO,4B_2O_3$.[180]

Few ternary or higher anhydrous calcium borates are recorded in the literature. The system $CaO–SiO_2–B_2O_3$ has been studied fairly extensively[192, 207–9] and found to have large areas of immiscibility.

Figure 7 shows the crystallization in the system; it will be noticed that two calcium borosilicates are shown crystallizing: $CaO,B_2O_3,2SiO_2$ and $5CaO,B_2O_3,SiO_2$.[209] The former of these is shown as the mineral *danburite.* Figures 8–19 show binary systems comprising various solid phase pairs.[209] It is reported that synthetic danburite may be crystallized from borosilicate solutions rich in calcium and carbon dioxide having a pH 8·0–8·5 in a hydrothermal reaction at 280–350°C.[218]

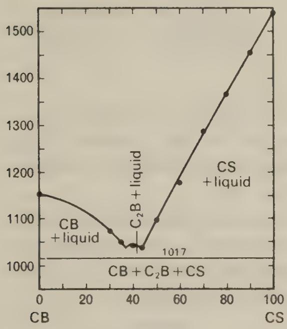


FIG. 8.—The join $CaO,B_2O_3–CaO,SiO_2$[209]

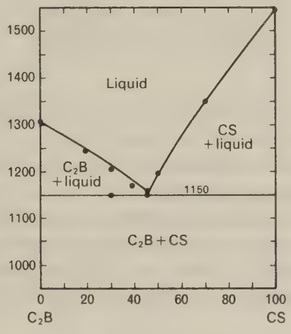


FIG. 9.—The system $2CaO,B_2O_3–CaO,SiO_2$[209]

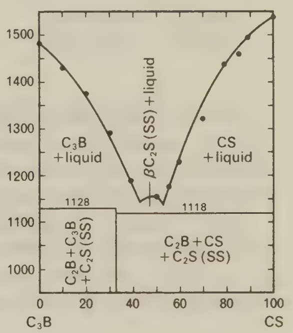


FIG. 10.—The join $3CaO,B_2O_3–CaO,SiO_2$[209]

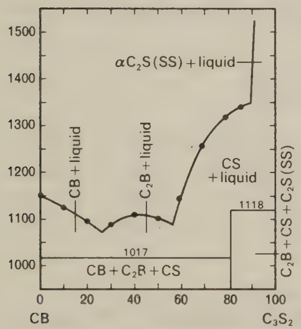


FIG. 11.—The join $CaO,B_2O_3–3CaO,2SiO_2$[209]

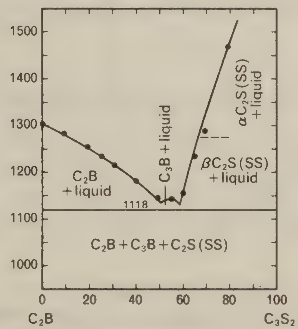


FIG. 12.—The join $2CaO,B_2O_3–3CaO,2SiO_2$[209]

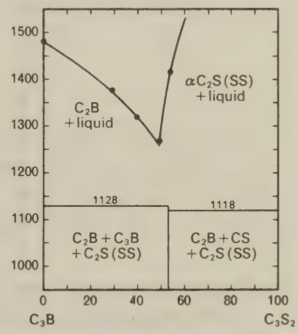


FIG. 13.—The join $3CaO,B_2O_3–3CaO,2SiO_2$[209]

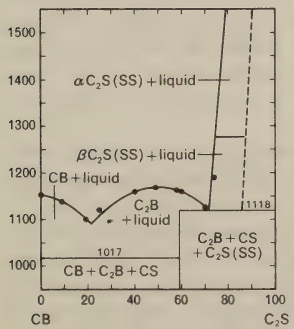


FIG. 14.—The join $CaO,B_2O_3–2CaO,SiO_2$[209]

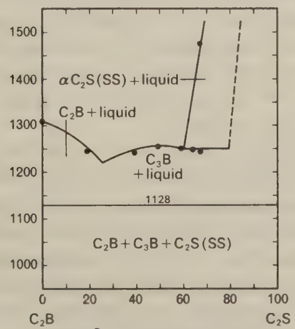


FIG. 15.—The join $2CaO,B_2O_3–2CaO,SiO_2$[209]

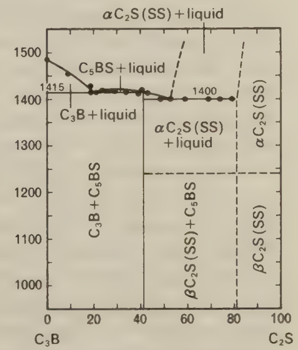


FIG. 16.—The system $3CaO,B_2O_3–2CaO,SiO_2$[209]

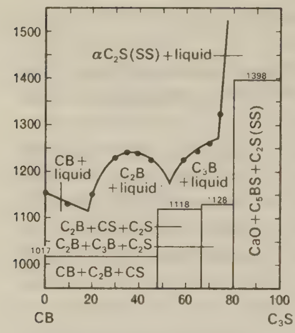


FIG. 17.—The join CaO,B_2O_3–$3CaO,SiO_2$[209]

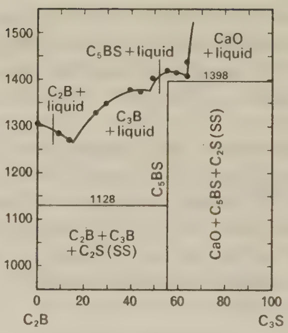


FIG. 18.—The join $2CaO,B_2O_3$–$3CaO,SiO_2$[209]

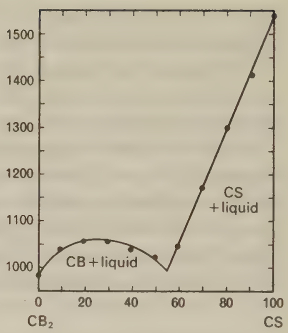
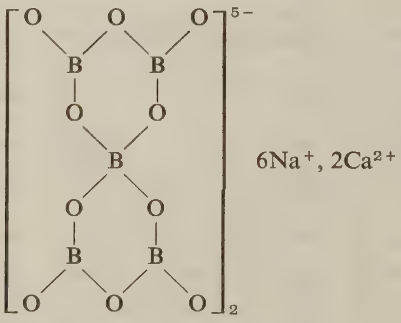


FIG. 19.—The join $CaO,2B_2O_3$–CaO,SiO_2[209]

There are three references to borates in the Na_2O–CaO–B_2O_3 system. $Na_2O,2CaO,B_2O_3$ is mentioned as reacting with sodium carbonate to give mixed crystals to the extent of 10%.[211] Its structure is quoted as belonging to the order of insular non-ring borates having independent polyanions.[63]

Borax reacts with calcium sulphate with the production of a phase identified as $Na_2O,2CaO,4B_2O_3$.[188] Recently a well defined borate of the formula $3Na_2O,2CaO,4B_2O_3$ has been crystallized from the Na_2O–CaO–B_2O_3 system. It has a melting point of 882°C and a density of 2·19 g cm^{-3} at 25°C. The formula:



has been postulated. X-Ray data are available.[187]

$2CaO,Al_2O_3,B_2O_3$ and CaO,Al_2O_3,B_2O_3 have also been synthesized[212, 229] and the structure of the latter discussed.[212] Tetragonal $Ca_2Mg(BO_3)_2$ has been synthesized.[659]

The mineral *nordenskiöldine* was synthesized in an autoclave by hydrothermal reaction of lime, stannic oxide and boric acid or borax.[87] The formula is CaO,SnO_2,B_2O_3; analogues of this compound are formed by substituting the oxides of ferrous iron, magnesium, barium or manganese for the calcium oxide. Borates of the type $M^{2+}M^{4+}(BO_3)_2$, where m = Mg, Ca, Sr, Ba, Cd, Mn or Co and M = Sn or Zr, have been synthesized from the melts.[658] The structure is reported to be analogous to those of $Na_2O,2CaO,B_2O_3$[63, 213] and dolomite.[10]

The compound $2CaO,P_2O_5,B_2O_3$ may be prepared by heating $CaHPO_4,2H_2O$ with boric acid for 2 hours at 600°C and then for 3 days at 900°C. By replacing the phosphate by arsenate the analogous arsenic compound $2CaO,As_2O_5,B_2O_3$ is formed.[129] These compounds have been characterized by X-ray analysis and differential thermal analysis and shown to be isotypical with the corresponding strontium compounds. They are stable to methyl alcohol, but are decomposed by water and dissolved by dilute acids.[129, 190] α-$Ca_3(PO_4)_2$ does not dissolve in molten boric oxide but the β-modification does to the extent of almost 20 mol.-% at 900°C.[86]

A compound of the formula $Ca[B(SO_4)_2]_2$ has been formed by reacting calcium

Table II.—Thermodynamic Properties of Calcium Borates

	ΔS, cal/deg/mole	ΔF, cal/mole	ΔH, cal/mole	Heat of solution in N–HCl at 298·16 K, cal/mole[185]
(Formation from oxides, at 298·16 K.[184])				
$3CaO,B_2O_3$	$2{\cdot}4 \pm 0{\cdot}7$	$-60{,}720 \pm 210$	$-6{,}000 \pm 40$	$-82{,}423 \pm 12$
$2CaO,B_2O_3$	$2{\cdot}7 \pm 0{\cdot}5$	$-46{,}570 \pm 150$	$-45{,}760 \pm 30$	$-50{,}287 \pm 20$
CaO,B_2O_3	$2{\cdot}6 \pm 0{\cdot}3$	$-30{,}200 \pm 90$	$-29{,}420 \pm 20$	$-20{,}259 \pm 8$
$CaO,2B_2O_3$	$-3{\cdot}3 \pm 0{\cdot}5$	$-41{,}950 \pm 150$	$-42{,}930 \pm 20$	$-10{,}080 \pm 10$
(Formation from elements, at 298·16 K.[184])				
$3CaO,B_2O_3$	$-136{\cdot}4 \pm 0{\cdot}6$	$-817{,}500$	$-858{,}200$	
$2CaO,B_2O_3$	$-111{\cdot}2 \pm 0{\cdot}5$	$-659{,}000$	$-692{,}100$	
CaO,B_2O_3	$-86{\cdot}3 \pm 0{\cdot}5$	$-498{,}300$	$-524{,}000$	
$CaO,2B_2O_3$	$-156{\cdot}2 \pm 0{\cdot}9$	$-833{,}700$	$-880{,}200$	

sulphate and sulphur trioxide with a large excess of boric acid; with an insufficient quantity of boric acid trisulphate borates are formed, such as $Ca[B_3O(SO_4)_3]$. These latter compounds are probably ionic, with high polymer anions.[11]

Compounds of the general formula $3MO,5B_2O_3,MX_2$ where M = Ca, Sr, Ba, Eu, Pb: X = Cl, Br have been produced.[373]

The results in Table II for heats of solution in hydrochloric acid were represented by the expression:

$$\Delta H = -3280 - 14{\cdot}60C$$

where C is the weight in grams of boric oxide dissolved in 1845·5 g of 1·000N hydrochloric acid.

Hydrated Calcium Borates

The first systematic study of the $CaO–B_2O_3–H_2O$ system was carried out by Sborgi[409] in 1913/14, and was later restudied by Nickolaev and Chelishcheva on a fully equilibrated system[119] (see Fig. 20). The quaternary system $Na_2O–CaO–B_2O_3–H_2O$ at 25°C (see Fig. 21) was studied by Kurnakova and Nikolaev[255], who discovered nine

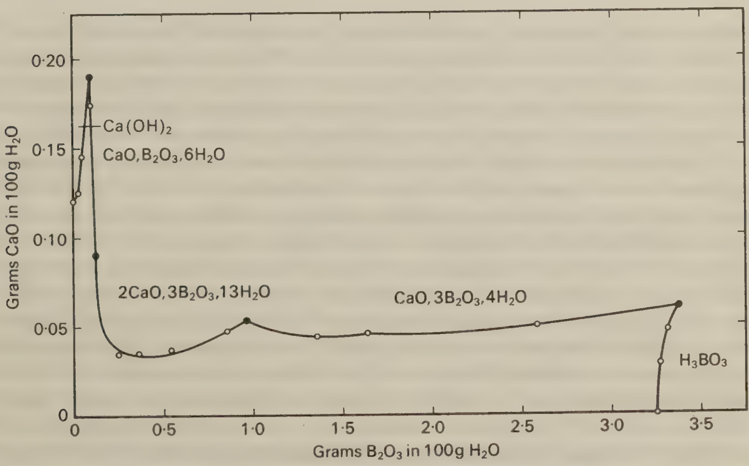


FIG. 20.—Solubility isotherm at 25°C of the system $CaO–B_2O_3–H_2O$[95]

Refs. p. 583

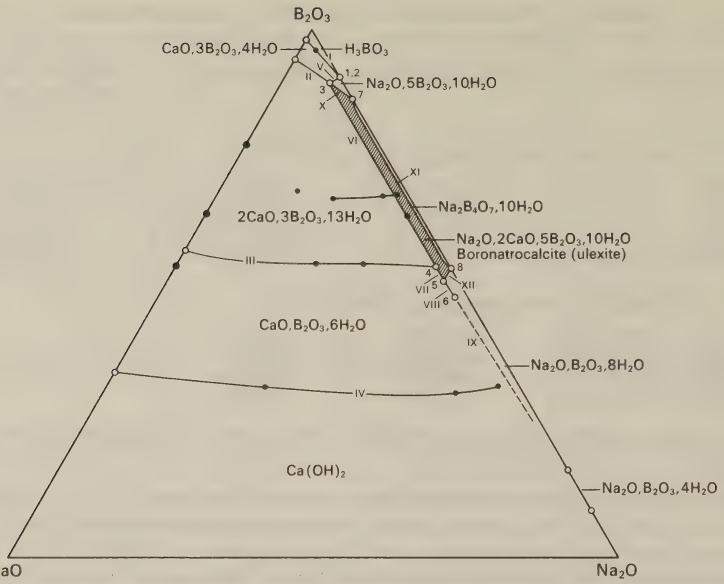


FIG. 21.—Isothermal crystallization at 25°C in the system $Na_2O–CaO–B_2O_3–H_2O$[95]

Lines of co-crystallization
I H_3BO_3–$CaO,3B_2O_3,4H_2O$
II $CaO,3B_2O_3,4H_2O$–inyoite
III Inyoite–$CaO,B_2O_3,6H_2O$
IV $CaO,B_2O_3,6H_2O$–$Ca(OH)_2$
V $CaO,3B_2O_3,4H_2O$–$Na_2O,5B_2O_3,10H_2O$
VI Inyoite–ulexite
VII $CaO,B_2O_3,4H_2O$–ulexite
VIII $CaO,B_2O_3,4H_2O$–$Na_2O,B_2O_3,8H_2O$
IX $Ca(OH)_2$–$Na_2O,B_2O_3,8H_2O$
X $Na_2O,5B_2O_3,10H_2O$–ulexite
XI $Na_2O,2B_2O_3,10H_2O$–ulexite
XII $Na_2O,B_2O_3,8H_2O$–ulexite

Eutonic points
1 Ulexite–$Na_2O,5B_2O_3,10H_2O$–$CaO,3B_2O_3,4H_2O$
7 $Na_2O,5B_2O_3,10H_2O$–borax–ulexite
8 $Na_2O,B_2O_3,8H_2O$–borax–ulexite

Transition points
2 $Na_2O,5B_2O_3,10H_2O$–$CaO,3B_2O_3,4H_2O$–ulexite
3 Inyoite–$CaO,3B_2O_3,4H_2O$–ulexite
4 Inyoite–$CaO,B_2O_3,6H_2O$–ulexite
5 $CaO,B_2O_3,6H_2O$–$Na_2O,B_2O_3,8H_2O$–ulexite
6 $CaO,B_2O_3,4H_2O$–$Ca(OH)_2$–$Na_2O,B_2O_3,8H_2O$

solid phases, four of which were calcium borates. Kesans reviewed the Russian work on this subject in 1955[21] and Nies and Campbell in 1962 gave a more general appraisal of the current work.[22] More recently Gode, an active worker in this field, has published a study on syntheses[214] with a review of the applications of calcium borates[215], and Nekrasov and Vlasova detected fourteen borates in a study of the $CaO–B_2O_3–H_2O$ system.[658] Gode later described conditions for the formation of calcium borates by an exchange reaction and presented his thesis in phase-diagram terms.[666] Outside Russia there was little work on calcium borate syntheses until recently, when Parkerson studied the $CaO–B_2O_3–H_2O$ system at temperatures ranging from 70 to 360°C.[180] Nikol'skii and Plyshevskii investigated the alkaline region at 95°C, proving $2CaO,B_2O_3,H_2O$ formation[639] and Shäfer studied the system at temperatures of 100–300°C (see Fig. 19)[267] as part of a study of the system $CaO–Al_2O_3–B_2O_3–H_2O$. Solid phases corresponding to the minerals *sibirskite*, *pandermite*, *fabianite*, *ginorite* and possibly *nobleite* or *gowerite* were identified as well as hitherto unknown hydrates 2:2:1 and 2:5:5 and the anhydrous 1:1 and 3:1 borates. Leibenguth studied the system $CaO–HF–B_2O_3–H_2O$.[216] Hanshaw studied the limited system $Na_2B_4O_7–Ca_2B_6O_{11}–H_2O$, constructing a semi-quantitative phase diagram theoretically derived using the symmetry of the equilibrium contents.[217] Christ *et al.* showed that all significant

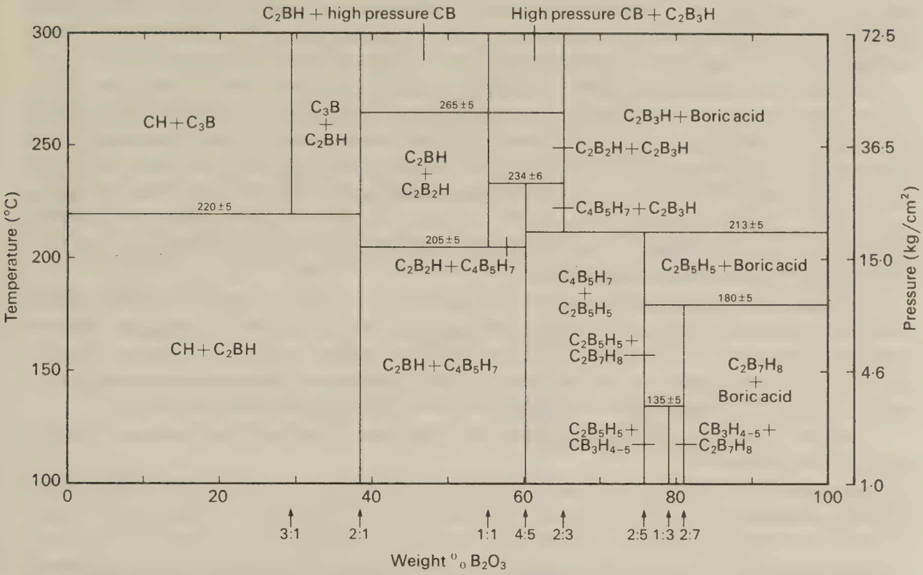


FIG. 22.—Solid phases in the system $CaO–B_2O_3–H_2O$ at 100–130°C
($C = CaO$; $B = B_2O_3$; $H = H_2O$)[267]

hydrated borate assemblages in the system $Na_2O–CaO–MgO–B_2O_3–H_2O$ were expressible in three ternary composition diagrams.[101] The system $Na_2O–K_2O–MgO–CaO–B_2O_3–H_2O$ with NaCl or $MgCl_2$ has been studied at 25–70°C.[560]

A variety of hydrated calcium borates exist with distinct physical and chemical characteristics; these are all difficult to crystallize and usually are formed via an indeterminate amorphous borate.[218, 219] pH is an important factor in determining the type of borate formed.[220] For instance, in the system $CaO–B_2O_3–H_2O$ at 25°C the relationship is as follows:

pH	*Borate found*
5·5–6·5	1:3:4
7·21–9·32	2:3:13
9·65–11·4	1:1:6

Thus the size of the polyborate ion decreases as the pH increases. As is usual with the formation of compounds containing complex anions the cation also has a distinct effect on the structure of the polyborate ion[221] (cf. $MgO–B_2O_3–H_2O$ system).

Other parameters important in controlling the type of borate formed are temperature and presence of neutral salts. At 45°C the solid phases found in the $CaO–B_2O_3–H_2O$ system are 1:3:4, 2:3:9 and 1:1:4 hydrates[222] (cf. the phases at 25°C above). This effect is carried to the extreme when under high pressures and temperatures, anhydrous calcium borates are formed; reactions in the $CaO–B_2O_3–H_2O$ system between 70 and 360°C were studied and many compositions previously only known as natural minerals were synthesized.[180] More recent study at 95°C in the alkaline region showed *inter alia* the formation of $2CaO,B_2O_3,H_2O$.[639] The addition of sodium chloride (to the extent of 5%) to the $CaO–B_2O_3–H_2O$ system modified the pH ranges of stability of the solid phases as well as introducing the boronatrocalcite as a further solid phase.[223] Solid-phase reaction has been reported between borax and calcite or dolomite in the presence of sodium, potassium or lithium carbonate, with the assumed formation of calcium borates.[224]

Calcium borates react with cationic exchange resins ('Zeocarb 225') to give boric acid; it is reported that the exchange is quantitative.[225] Hot calcium borates will decompose slightly in the presence of steam, causing the volatilization of boric acid.[226] Both these facts have been considered in the production of boric acid, reviewed elsewhere. Thermal decomposition of calcium borates has been reviewed.[227]

Calcium borates hydrolyse in water, showing an appreciable 'apparent solubility'.[22] It is therefore not easy to remove traces of borate from water by precipitation as calcium borate; however, borates in low concentrations can be sorbed from sea water by treatment with calcined marble, magnesite or sintered lime and magnesia, CaO/MgO.[228] The solubility of various calcium borate minerals in solutions of sulphuric acid[166], hydrochloric acid[167] and nitric acid[164] have been studied and the mechanisms of solution deduced. Mutual solubility in the $Ca(NO_3)_2$–$Mg(NO_3)_2$–H_3BO_3–H_2O system has been studied.[232]

Thermodynamic properties have been derived for calcium borates of the general formula CaO,mB_2O_3,nH_2O.[186] Infra-red spectra for a number of calcium borates have been studied[233,649] and the X-ray diffraction patterns of the 2:3 borates investigated[234], the refinement of the various 2:3 calcium borate hydrate structures resulting.[235] Atomic co-ordinates in various calcium borates have been reported.[236]

Excellent Liesegang-ring phenomena are obtained from peptized calcium borates and barium borates.[237]

The action of alkalis on calcium borate ores has been studied with the aim of refining borates.[567]

$CaO,B_2O_3,\frac{1}{2}H_2O$. This borate appears in the CaO–B_2O_3–H_2O system at about 200°C (see Fig. 22).

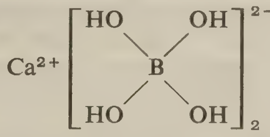
CaO,B_2O_3,H_2O. Known as the recently discovered mineral *korzhinskite*.[238]

$CaO,B_2O_3,2H_2O$. The dihydrate of calcium metaborate is formed as an amorphous powder by heating the hexahydrate at 105°C. The crystalline compound is reported as being formed by heating the anhydrous material or a 1:2·5 molar ratio of calcium oxide, boric acid and water at 180°C, or by holding the amorphous dihydrate at 105°C for several days.[203] However, the same workers revised views concerning the formation of the crystalline dihydrate by hydrothermal methods.[239] They found that at temperatures ranging from 100–190°C and $CaO:B_2O_3$ ratios between 1:1 and 1:3, mixtures of the 2:1:1 borate and pandermite (4:5:7) were produced. The thermal dehydration of the synthetic 1:1:2 borate has been studied, *inter alia*, with the 1:1:4 and 1:1:6 calcium borates.[568] Its dissolution rate in water has been measured and the suggestion made that it is a good slow-release fertilizer.[638]

The mineral *uralborite*, which corresponds to the same formula, is well substantiated and exists as clusters of hexagonal prismatic crystals with a density of 2·60. It has been characterized by X-ray powder diagrams and D.T.A. curves[240] and differentiated from *nifontovite* ($CaO,B_2O_3,2{\cdot}3H_2O$) and *frolovite* ($CaO,B_2O_3,3{\cdot}65H_2O$) by infra-red absorption spectra.[241] Another mineral *vimsite*, having the formula $CaO,B_2O_3,2{\cdot}2H_2O$, has been discovered in the form of elongated monoclinic crystals having a density of 2·54.[242] Its crystal structure has been described in detail.[243]

$CaO,B_2O_3,4H_2O$. Calcium metaborate tetrahydrate is formed in the same general manner as the hexahydrate, but at temperatures above about 30°C.[244] It may be obtained from the CaO–B_2O_3–H_2O system at 45°C in the form of rectangular crystals.[222] Needle-like crystals of the same material are also obtained by adding 4·4 g of $CaCl_2,6H_2O$ in 10 ml of water to a boiling solution of 15 g of borax ($Na_2O,2B_2O_3,10H_2O$) and 4 g of sodium hydroxide in 90 ml of water, and holding the amorphous precipitate at 75°C for 4–5 days.[245] Two industrial methods of producing tetrahydrate and hexahydrate, using as reactants hydrated lime, gypsum and borax, are described. In one case[244], borax (230 g) lime (47 g) and gypsum (98·5 g) are stirred together in a litre of water with some tetrahydrate seed at a temperature between 40 and 100°C producing a crystalline tetrahydrate after only 2 hours. Alternatively[247], a mixture of borax (450 g) and caustic soda (96 g) is dissolved in 900 cm^3 of water at 55°C and added to calcium hydroxide (22 g) and gypsum (50 g) in 100 g of water, to which a little tetrahydrate seed has been added; this process produces $CaO,B_2O_3,4H_2O$ in a crystalline form after 5 hours at 50°C. The addition of amorphous '$CaO,3B_2O_3,8H_2O$' to a potassium borate solution under certain conditions of concentration and pH is reported to give the crystalline tetrahydrate at room temperatures.[219] The tetrahydrate is also formed from sodium borate and calcium chloride solution, temperature (which should be below 20°C) as well as concentration and alkali ratio influencing the result.[665]

Work has been carried out using the 1:1:4 borate in glazes, where it can be applied without preliminary frittage.[248] The structure of the compound has been deduced conclusively as[249]:



with the calcium ion surrounded by eight co-ordinated oxygen atoms[250] in the same way as in the corresponding strontium salt, $SrO,B_2O_3,4H_2O$. Infra-red spectra confirm the presence of a tetrahydroborate ion by the B–OH deformation vibrations.[251] The crystals are reported to belong to the prismatic class of the monoclinic system.[249] Both α and β crystal modifications are known and the structure of α–$Ca[B(OH)_4]_2$ is described as orthorhombic.[252–3] Differential thermal analysis shows a strong dehydration effect at 180°C and an exothermic peak at 700°C.[248] A thermogram on a single crystal has been studied and shows similarity to the mineral *frolovite* ($CaO,B_2O_3,3{\cdot}65H_2O$).[245] The crystal structure of this mineral has been determined, although the authors quote a tetrahydrate formula.[651] Further work on the thermal dehydration of the synthetic 1:1:4 borate has been carried out.[568]

$CaO,B_2O_3,5H_2O$. This was only known as the mineral *pentahydroborite* until synthesized by Russian workers.[653] The crystal structure indicated $Ca[B_2O(OH)_6],2H_2O$ with triclinic habit and $d = 2{\cdot}02$ (calc.).

$CaO,B_2O_3,6H_2O$. This compound is the most easily formed and best known of all crystalline synthetic calcium borates. In addition to the methods used for the production of the tetrahydrate (but at lower temperatures)[219, 244, 245, 247] the hexahydrate is reported as being formed in the following ways.

Studies of the systems $CaO–B_2O_3–H_2O$[92, 119], $Na_2O–CaO–B_2O_3–H_2O$[255] and $CaO–NaCl–B_2O_3–H_2O$[223] at 25°C all produced the characteristic hexagonal crystals. A product contaminated with calcium hydroxide was produced by adding 3% by weight of fresh calcium oxide to a 10% sodium chloride solution saturated with boric acid.[109] Control of pH was found to be important and the generalization made that pure 1:1:6 can be prepared in a few hours by taking a large excess of a $B_2O_3:Na_2O$ solution of molar ratio 0·93–0·5 and treating it with calcium chloride. The pH does not appreciably change and the Ca^{2+} ions are precipitated as $CaO,B_2O_3,6H_2O$.[246, 256] Fairly large crystals were obtained by allowing calcium chloride to diffuse into a solution of $B_2O_3:NaO$ ratio 0·6.[257–8] It was found that temperature, the $Na_2O:B_2O_3$ ratio and the amount of calcium chloride added influence the synthesis.[665] Hexahydrate formation is favoured at above 35°C.

It was deduced from conductivity and cryoscopic measurements that in aqueous solution the borate hydrolyses according to:

$$CaO,B_2O_3,6H_2O + H_2O \rightarrow Ca^{2+} + 2OH^- + 2H_3BO_3 + 3H_2O.^{23}$$

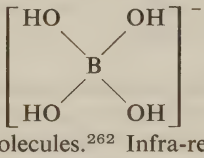
If reacted with borax the metaborate hexhydrate forms *ulexite* or *probertite*, depending upon the conditions shown on the following page[259]:

$$2[Na_2O,2B_2O_3,10H_2O]+2[CaO,B_2O_3,6H_2O] \xrightarrow[\substack{20^\circ\ 119\ \text{days}\\ 40^\circ\ \ 60\ \text{days}}]{}$$

$$\underset{\textit{ulexite}}{Na_2O,2CaO,5B_2O_3,16H_2O}+Na_2O,B_2O_3+16H_2O \xrightarrow[105^\circ\ 8\ \text{days}]{}$$

$$\underset{\textit{probertite}}{Na_2O,2CaO,5B_2O_3,10H_2O}+Na_2O,B_2O_3+22H_2O.$$

In the $CaO–B_2O_3–H_2O$ system it takes 36 days at 25°C before the hexahydrate is in stable equilibrium with its liquid phase, which contains 0·195% of CaO and 0·108% of B_2O_3.[147] If the hexahydrate is heated at 105°C an amorphous compound is formed corresponding to the formula $CaO,B_2O_3,2H_2O$, which may be converted into the crystalline form by prolonged heating in water at 105°C. The same dihydrate is crystallized by heating the hexahydrate at 180°C with water.[203]

By X-ray diffraction the crystals are found to belong to the rhombo-prismatic class[260] of the monoclinic system.[261] The unit cell contains 2 boron atoms each tetrahedrally surrounded by 4 oxygen atoms. Eight oxygen atoms surround each calcium atom. The  ions are bound together by means of a Ca^{2+} ion and 2 water molecules.[262] Infra-red studies agree with this structure and not $Ca[B_2O(OH)_6],3H_2O$.[263] The density of the crystals has been determined as 1·870 experimentally and 1·878 by calculation.[263] A thermogravimetric investigation of single crystals of the hexahydrate has been carried out.[245, 568] $CaO,B_2O_3,6H_2O$ was reported to dehydrate with the formation of a dihydrate as intermediate[663], but other workers found a first-stage dehydration to a tetrahydrate (≤120°C) followed by a decomposition of the $Ca[B(OH)_4]_2$ structure in the second stage (120–520°C), leaving an anhydrous $CaO–B_2O_3$ mixture.[668] An O D disordered modification of the 1:1:6 borate has recently been discovered and may be represented by $Ca(B(OH)_4)_2.2H_2O$.[569] A polytype of the layered borate $CaB_2O_4,6H_2O$ has been reported.[650]

$CaO,2B_2O_3,\frac{1}{2}H_2O$. Each unit cell of this triclinic compound was found to consist of two units of $Ca_2[B_8O_{13}(OH)_2]$.[655] The structure has a layer character and consists of bent chains of Ca polyhedra cemented by a B–O skeleton of BO_3 triangles and BO_4 tetrahedra.

$CaO,2B_2O_3,xH_2O$. The compound $CaO,2B_2O_3,6H_2O$ has been reported to be formed by the action of calcium chloride on borax in solution[264], but under normal conditions it is highly unlikely that it is formed as crystalline compound. The minerals *bechilite* ($CaO,2B_2O_3,4H_2O$) and *hayesine* ($CaO,2B_2O_3,6H_2O$) have been reported, but there is little evidence to support their existence.

$CaO,3B_2O_3,2H_2O$. Fine crystals with a density of 2·51 ± 0·04 corresponding to $CaO,3B_2O_3,2H_2O$ were prepared by hydrothermally heating gowerite ($CaO,3B_2O_3,5H_2O$) with boric acid at temperatures between 170 and 360°C[180], or a mixture of lime and boric acid at 260°C.[265]

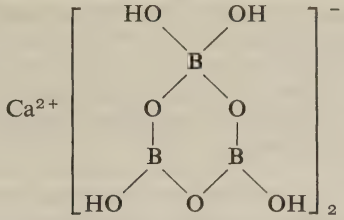
$CaO,3B_2O_3,3H_2O$. Only known as the mineral *volkovskite.*

$CaO,3B_2O_3,4H_2O$. This compound is a stable phase in the $CaO–B_2O_3–H_2O$ system at 25°C[119] and at 45°C.[222] It is also formed from an aqueous mixture of lime (CaO) and boric acid at 60°C[266], and occurs as a solid phase in the systems $Na_2O–CaO–B_2O_3–H_2O$[255] and $CaO–NaCl–B_2O_3–H_2O$[223] at 25°C at a pH of 5·5–6·5. Hydrothermal treatment of *meyerhofferite* ($2CaO,3B_2O_3,7H_2O$) in boric acid solution at 85–250°C produced crystals of both the tetrahydrate and pentahydrate together with *ginorite* ($2CaO,7B_2O_3,8H_2O$).[180]

The 1:3:4 calcium borate is also found as the mineral *nobleite.*

The tetrahydrate is monoclinic[22] and has a density of 2·09.[21] The refractive indices of the crystals have been studied[222] and the effect of heat on the crystals commented on.[94, 222]

The structure of the synthetic compound is classified in the structural groups as belonging to the 'single-ring borates with independent polyions'[63], i.e.



The mineral nobleite appears to have a structure which does not correspond to this.[270]

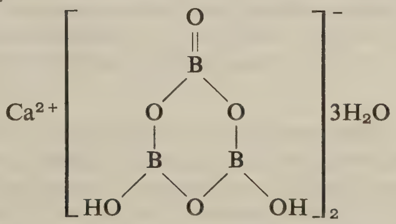
$CaO,3B_2O_3,5H_2O$. The pentahydrate is not found as a solid phase in the CaO–B_2O_3–H_2O system below 60°C but has been formed from lime and boric acid in aqueous media at 100°C; the ratio $CaO:H_3BO_3$ is critical.[266]

The compound may be formed in 60% yield by reacting 40 g of calcium acetate with 80 g of boric acid in 200 ml of water, pouring the mass of tiny needle-like crystals into 2 litres of water, stirring and leaving overnight.[269] Alternatively, calcium chloride or nitrate may be mixed with a 5:3 (by weight) mixture of borax and boric acid in water and left for several weeks; an amorphous material analysing as $CaO,3B_2O_3,5H_2O$ is formed.[109] A similar synthesis was described later.[664]

The pentahydrate is also formed hydrothermally at 85–250°C from meyerhofferite and boric acid (see tetrahydrate, above[180]). The mineral gowerite has the formula $CaO,3B_2O_3,5H_2O$. It appears that there is no simple hydration/dehydration relationship between nobleite ($CaO,3B_2O_3,4H_2O$) and gowerite.[270]

Hydrolysis of the hexaborate takes place via the unstable tetraborate $[B_4O_7]^{2-}$ and diborate $[BO_2]^-$ ions. Boric acid moderates hydrolysis, whereas dilution facilitates it.[23] The mobility of the anion in water at 25°C is the same for $MgO,3B_2O_3,7H_2O$, $SrO,3B_2O_3,5H_2O$ and $CaO,3B_2O_3,5H_2O$, being 34 mho/cm². The material has a density of 2·12 and a 'solubility' of 6·03 g/l. It melts at 900°C and loses its first mole of water at 85°C, the second at 85–110°C, the third and fourth at 230°C and the last at 480°C.[269, 663] X-Ray data, crystal form, and differential thermal analysis have been studied[271] and the infra-red spectra of the compound investigated.[272]

The structure of gowerite has been placed in the structural group of 'chain borates with single rings'[63], i.e.



No structural data are available for the synthetic compound.

$2CaO,B_2O_3,H_2O$. This compound is prepared in admixture with pandermite from the dehydrated 1:1:6 or 1:1:4 compounds or a mixture of calcium oxide and boric acid by hydrothermal reaction at temperatures between 100–190°C.[239] Other syntheses, apparently yielding uncontaminated products, are summarized as follows[203]:

$$\left.\begin{array}{rl}\text{(i)} & Na_2O,2CaO,B_2O_3\\ \text{(ii)} & 2CaO,B_2O_3\\ \text{(iii)} & CaO+H_3BO_3 \text{ in equal amounts}\\ \text{(iv)} & CaO,B_2O_3,2H_2O+NaOH\\ \text{(v)} & CaO,B_2O_3,2H_2O+CaO\end{array}\right\}+H_2O \xrightarrow{180^\circ C} 2CaO,B_2O_3,H_2O.$$

$$\left.\begin{array}{ll}\text{(vi)} & \text{CaO} + \text{H}_3\text{BO}_3 \text{ in equal amounts} \\ \text{(vii)} & \text{Concentration of Ca(OH)}_2 + \\ & \text{Na}_2\text{O,B}_2\text{O}_3 \text{ solutions at pH 12} \\ & \text{excluding CO}_2\end{array}\right\} + H_2O \xrightarrow{100^\circ C} 2CaO,B_2O_3,H_2O.$$

$2CaO,B_2O_3,H_2O$ is also found in nature as the mineral *sibirskite*[273] whose X-ray data are identical with the synthetic compound.[203, 204] It exists as rhombic crystals with a density of 2·58. Its formation in the alkaline region of the $CaO–B_2O_3–H_2O$ system was proved by X-ray analysis.[639] The synthetic compound starts to lose water at 200°C and dehydration is complete at 400°C[203]; these data have been checked by a differential thermal analysis carried out on *sibirskite*.[273]

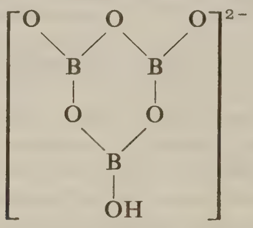
$2CaO,3B_2O_3,H_2O$. Hydrothermal reactions are the best way of producing this compound, recognized as being identical with *fabianite*.[274] Inyoite in contact with water at 400°C for several days[22] produces this compound, as do the following reactions[180]:

$$\begin{array}{l}2{:}3{:}7 + H_3BO_3 \text{ solution} \\ \text{(meyerhofferite)}\end{array} \xrightarrow{85-250^\circ C}{:}\ 2CaO,3B_2O_3,H_2O \text{ with} \left\{\begin{array}{l}1{:}3{:}4 \\ 1{:}3{:}5 \\ 2{:}7{:}8 \\ 3{:}7{:}3\end{array}\right.$$

$$\begin{array}{l}1{:}3{:}5 + H_2BO_3 \text{ solution} \\ \text{(gowerite)}\end{array} \xrightarrow{170-360^\circ C} 2CaO,3B_2O_3,H_2O \text{ with} \left\{\begin{array}{l}2{:}7{:}8 \\ 1{:}3{:}2 \\ 4{:}7 \text{ (anhydrous)}\end{array}\right.$$

$$\begin{array}{l}2{:}7{:}8 + H_3BO_3 \text{ solution} \\ \text{(ginorite)}\end{array} \xrightarrow{350^\circ C} 2CaO,3B_2O_3,H_2O \text{ with } 4{:}7 \text{ (anhydrous)}$$

Both the synthetic compound[275] and the mineral[276] are shown to belong to the order of sheet borates with cross-linked 'colemanite chains' incorporating single rings:



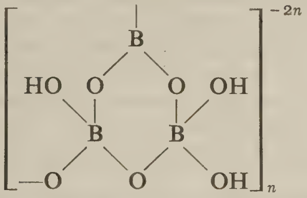
The infra-red spectra agree with the formula $Ca[B_3O_5(OH)]$ and give evidence of planar BO_3 groups and BO_4 tetrahedra.[274] The crystalline structure of fabianite derived by Patterson and electron-density syntheses is shown to be monoclinic, and the calculated density is given as 2·788 g/cm³.[570] Indexed powder X-radiograms for fabianite are recorded and compared with that of the orthorhombic synthetic compound.[571]

$2CaO,3B_2O_3,5H_2O$. Colemanite, the best known calcium borate found naturally, has this composition. Other 2:3 calcium borates of different hydration states form a distinct series: inyoite ($13H_2O$), a synthetic compound ($9H_2O$), meyerhofferite ($7H_2O$), colemanite ($5H_2O$), and fabianite ($1H_2O$). Van't Hoff's synthesis of colemanite has been repeated[21] successfully, and it was shown that inyoite could be transformed into colemanite by heating it with half its weight of colemanite seed over a period of 8 days at 100°C, 15 days at 50°C or 20 days at 20°C.[132] More recently a deuterated colemanite has been produced by two methods[277]:

(1) (*a*) 10 g anhydrous borax dissolved in 100 ml D_2O at 70°C and cooled gave $Na_2O,2B_2O_3,10D_2O$. (*b*) 3·34 g $Na_2O,2B_2O_3,10H_2O$ and 1·34 g $CaSO_4,2H_2O$ heated and agitated in 200 g D_2O at 68°C gave $2CaO,3B_2O_3,7D_2O$ (1·13 g). (*c*) 1·13 g $2CaO,3B_2O_3,7D_2O$, 1·93 g $Na_2O,2B_2O_3,10D_2O$ and 0·12 g colemanite seed in 125 g D_2O formed, after 56 days, with a 100% conversion, $2CaO,3B_2O_3,5D_2O$.

(2) $Na_2O,2B_2O_3,10D_2O + Na_2SO_4 + CaCl_2 + D_2O \xrightarrow{\text{(conditions as (1))}}$ 50% conversion into $2CaO,3B_2O_3,5D_2O$.

Colemanite has interesting ferroelectric and pyroelectric characteristics. A synthetic colemanite produced by controlled dehydration of a higher hydrate has a lower Curie temperature than the mineral.[278] Investigations have been carried out to study the structural alterations that take place during its paramagnetic changeover at the Curie temperature.[279] It has been shown that hydrogen bonding makes an important contribution to the phenomenon of ferroelectric transition, which was confirmed by some work on the accurate positioning of the protons in the colemanite structure.[280] The structure is defined as belonging to the 'order of chain borates containing single rings'[63], in which the unit is[281, 281a]:



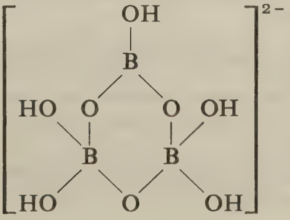
The stable characteristics of colemanite may be explained by this polymeric structure, an explanation confirmed by the lower stability of the higher hydrates, which do not polymerize in the same way. Other physical studies of colemanite have included D.T.A.[141], n.m.r.[283], and miscellaneous optical investigations.[282, 284, 285] When heated, colemanite decrepitates violently, losing all its water at 480°C.[161] The thermal decomposition of $2CaO,3B_2O_3,nH_2O$-type calcium borates has been studied.[656] The solubility of colemanite in water is 0·18 wt.-% B_2O_3 at 25°C and 0·38 wt.-% B_2O_3 at 100°C.[112] Other work on the hydrolysis of colemanite shows that it converts very slowly into pandermite ($4CaO,5B_2O_3,7H_2O$).[132]

Colemanite being a principle raw material for the production of boric acid by decomposition with mineral acids, the kinetics of solution have been studied in detail. The maximum rate of solution of colemanite is found using 0·2–5% hydrochloric acid[575]; above 20% hydrochloric acid the rate levels out.[166, 167] The dissolution curves for sulphuric acid[168] and nitric acid[164] are similar to that for hydrochloric acid and show that the reaction is controlled by diffusion.[167] The production of boric acid from colemanite is discussed in detail elsewhere. Patents exist for the production of boric acid from colemanite and all the mineral acids, sulphur dioxide, ammonia and carbon dioxide, silica and ion-exchange resins. Calcium borate solutions are formed directly from colemanite reacted with boric acid containing 100–240 g of boric acid per kg of solution.[572]

A mixture of colemanite and portland cement in a 4:1 ratio can give many large crystals of the 1:1:6 calcium borate.[286]

$2CaO,3B_2O_3,7H_2O$. This compound is known naturally as the mineral meyerhofferite. The only recent syntheses are as an intermediate phase in the production of deuterated colemanite[277] (see above) and by the reaction of borax with calcium iodate in water at 70°C.[180]

The structure of meyerhofferite has been studied extensively in comparison with colemanite and inyoite, and it is generally accepted that the anion present in the structure is[287, 280]:



From the thermodifferential curve another worker suggests a formula $Ca_2B_6O_9(OH)_4,5H_2O$ as there is a rapid loss of 5 molecules of water between 170 and 200°C followed by a slow loss of the remaining 2 molecules of water to give the anhydrous product at 450°C.[161]

Meyerhofferite reacts with boric acid solutions at temperatures between 85° and 250°C to give the following calcium borate hydrates: 1:3:4 (nobleite), 1:3:5 (gowerite), 2:3:1 (synthetic), 2:7:8 (ginorite) and 3:7:3 (synthetic).[180]

$2CaO,3B_2O_3,8H_2O$. This hydrate was formed as a high-surface-area precipitate on mixing solutions of calcium chloride and borax.[661]

$2CaO,3B_2O_3,9H_2O$. This is the only purely synthetic hydrate of the 2:3 calcium borates. It is formed as a solid phase in the $CaO–B_2O_3–H_2O$ system at 45°C and crystallizes in the form of elongated rectangles whose refractive indices and thermograms show it to be a distinct hydrate.[222] It is also formed when fragments of ulexite ($NaO,2CaO,5B_2O_3,16H_2O$) are held in water at 50°C for about a month; very good crystals are formed by treating ulexite with a large excess of water at 40–45°C.[259, 288] Analogously this hydrate is formed by hydrolysis of $K_2O,CaO,4B_2O_3,12H_2O$ at 25°C.[573]

The structure of the anion is the same as that postulated for meyerhofferite and inyoite, i.e. $[B_3O_3(OH)_5]^{2-}$.[288]

$2CaO,3B_2O_3,13H_2O$. The highest hydrate of the series is inyoite, formed as solid phase in the $CaO–B_2O_3–H_2O$[289], $NaCl–CaO–B_2O_3–H_2O$[223] and $Na_2O–CaO–B_2O_3–H_2O$[255] systems at 25°C. Whereas the pH field of formation in the former system is 7·21–9·32, in the system with 5% of sodium chloride added the pH of formation is between 8·0 and 9·65.[223] Accelerated methods of formation under laboratory conditions have been studied, with particular reference to the effect of impurities.[290, 291] Inyoite is also formed from a non-crystalline 1:3:8 calcium borate hydrate in a potassium borate solution at room temperature.[219] Alternatively a saturated solution of kaliborite reacts with gypsum in water to give a mixture of inyoite and hydroboracite.[132] A gypsum solution treated with 250 ml of a saturated borax solution and allowed to stand for 9 months produces crystalline inyoite.[292] A reaction time of only 2 weeks is needed for inyoite to form by treating ammonium magnesium borate with a saturated solution of calcium chloride.[21]

The solubility of inyoite in water at 25°C is 0·15% B_2O_3.[134] It hydrolyses, like the majority of calcium borates, and after 15 days at 20°C is transformed into pandermite ($4CaO,5B_2O_3,7H_2O$)[132] (see colemanite, above). The solubility in saturated gypsum solutions and sodium chloride solutions at 25 ± 2°C has been determined; in the former the solubility increases to 0·21% B_2O_3.[46] The kinetics of solution of inyoite in water[112, 123], hydrochloric acid[165, 167] and nitric acid[164] have been investigated (see colemanite). The dissolution of inyoite in methanol, acetic acid, citric acid and tartaric acid (at 25–50°C) is governed by pH and by the formation of surface films.[293]

As with the 1:1:6 and 1:3:4 calcium borates an endothermic effect is shown by heating inyoite up to 450°C, and at 600–700°C an exothermic effect shows a change of state.[94] More detailed studies of isothermal dehydration[294, 574] and differential thermal analysis[141] have been carried out.

The structure of inyoite is based on the $[B_3O_3(OH)_5]^{2-}$ ring-structure ion[280, 295] (see $2CaO,3B_2O_3,7H_2O$, above).

The solid-phase reactions of $2CaO,3B_2O_3,13H_2O$ with sodium carbonate and bicarbonate have been studied[296] and concurrently the solubility of the reaction products.[297] The transition of non-crystalline calcium borate to inyoite has been studied by measurements of the boron isotopic composition.[442]

$2CaO,5B_2O_3,5H_2O$. This borate appears in the $CaO–B_2O_3–H_2O$ system between 135° and 200° approximately (see Fig. 22).

$2CaO,5B_2O_3,H_2O$. Hydrothermal reaction of a lime and boric acid mixture ($B:Ca = 9{\cdot}0$) at 190°C (~13 atm) gives this compound, which has a density of 1·82. At temperatures ranging between 295 and 362°C and $B:Ca = 20$ another form of this compound is reported to be formed, with $d = 2{\cdot}14$.[298]

$2CaO,7B_2O_3,8H_2O$. This compound is also known as the mineral ginorite and can be formed by hydrothermal reaction of meyerhofferite (2:3:7) and boric acid at 85–250°C, or gowerite (1:3:5) and boric acid at 170°C.[180]

From X-ray studies of ginorite[299, 300] a probable structure of the following composition, containing two different polyions, was postulated[63]:

$$Ca_2[B_4O_5(OH)_4][B_5O_6(OH)_4]_2,2H_2O$$

Differential thermal analysis has been carried out on this hydrate.[301]

$3CaO,4B_2O_3,2H_2O$. This compound is known only as the rare mineral *tyretskite.*

$3CaO,7B_2O_3,3H_2O$. This compound is formed when a mixture of lime and boric acid at 200–350°C or meyerhofferite and boric acid is reacted hydrothermally at 85–250°C.[180]

$4CaO,5B_2O_3,7H_2O$. A compound closely corresponding to this formula has been produced by adding to a mixture of 200 ml of 0·5N sodium hydroxide and 200 ml of 0·5N boric acid, 100 ml of N calcium chloride at room temperature. The solid phase, when dried at 50°C, was found to be somewhat more soluble than the mineral *pandermite* or *priceite* ($4CaO,5B_2O_3,7H_2O$)[302] and is quite likely to have been one of many variable-composition amorphous borates. A compound apparently identical to pandermite was formed as a solid phase in the $CaO–B_2O_3–H_2O$ system at 200–350°C and by hydrothermal reaction of borax and gypsum at 125–340°C.[180] Pandermite can be synthesized by slow hydrolysis of ulexite ($Na_2O,2CaO,5B_2O_3,16H_2O$)[259], inyoite or colemanite.[132]

The solubility of pandermite at 25°C is variously described as 'slight'[303], 0·04% B_2O_3[134], and 0·20%.[112] Its solubility in boric acid solution decreases, then increases, as the boric acid concentration increases. The heat of solution increases with increasing boric acid concentration; it is slightly negative at <38°C but becomes slightly positive at higher temperatures. The heat of activation at 50 and 100°C is the same in water or boric acid solution.[304] Details of the dehydration pattern of pandermite differ in two publications.[305–6] A differential thermal analysis has been carried out on pandermite.[306]

The structure of pandermite has until recently been purely conjectural, but in 1966 it was assigned to the order of 'sheet borates'[63] containing double-ring anions, i.e. $[B_5O_8(OH)_3]^{4-}$.[307] It has also been suggested that the compound may have the formula $4CaO.5B_2O_3,7\frac{1}{2}H_2O(8CaO.10B_2O_3,15H_2O)$; dehydration produces an intermediate phase: $4CaO.5B_2O_3,3\frac{1}{2}H_2O(8CaO,10B_2O_3,7H_2O)$.[663]

$4CaO,5B_2O_3,20–21H_2O$. Known only as the mineral *tertchite.*

Hydrated Calcium Double Borates

Calcium Ammonium Borate

$(NH_4)_2O,CaO,4B_2O_3,12H_2O$. This is a well characterized compound, formed if 12 g of boric acid in 200 ml of water are treated with 17·5 ml of concentrated ammonia solution and 2·2 g of calcium chloride in 20 ml of water. At first an amorphous white precipitate forms, which, after about 3 days, crystallizes completely. The compound has $d_{25} = 1{\cdot}650$; it has a rhombic bipyramidal structure with one centre of symmetry.[308] Further details of the formation of this compound, together with its potassium analogue and ulexite, have been reviewed, including details of crystal forms, densities and optical properties.[215] The compound loses its ammonia and some water at 88°C; at 100°C 10 molecules of water are driven off, but it is not until 429°C that the compound is completely dehydrated.[308]

Calcium Sodium Borates

$Na_2O,2CaO,5B_2O_3,10H_2O$. This compound is commonly found crystallizing out as a troublesome scale in borax refineries; it is also known as the mineral *probertite.* It may be synthesized by heating a mixture of 4·9 g of $Na_2O,2B_2O_3,10H_2O$ and 15 g of $CaO,B_2O_3,6H_2O$ in 9 g of water for 8 days at 105°C.[259] Ulexite transforms to it when probertite seed is added to moistened ulexite and the material held at 80–100°C for about 4 weeks.[22]

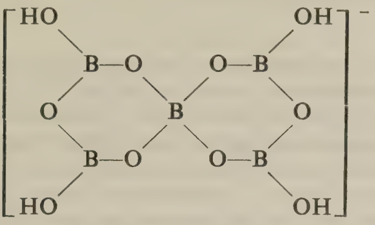
Crystals of probertite belong to the monoclinic system and have a structural formula containing a double-ring anion, linked in chains[63], corresponding to $[B_5O_7(OH)_4]^{3-}$. The complete formula is therefore given as $NaCa[B_5O_7(OH)_4],$-$3H_2O$.[309, 310]

$Na_2O,2CaO,5B_2O_3,16H_2O$. This compound is formed as triclinic needle-like crystals in both the $Na_2O–CaO–B_2O_3–H_2O$[255] and $NaCl–CaO–B_2O_3–H_2O$[223] systems at 25°C. The compound is identical to the mineral *ulexite*[259] and is prepared in a similar way to probertite, by keeping a mixture of 13·5 g of $Na_2O,2B_2O_3,10H_2O$ and 4·15 g of $CaO,B_2O_3,6H_2O$ in 100 g of water for 119 days at 20°C, or 60 days at 40°C.[259] More rapid synthesis (in 24 hr) is obtained by adding calcium chloride to a solution containing a $B_2O_3:Na_2O$ ratio equal to 1:7, and using a sufficient excess of borate to obtain a constant pH.[21] Other attempts have been made to synthesize ulexite.[114, 215, 311]

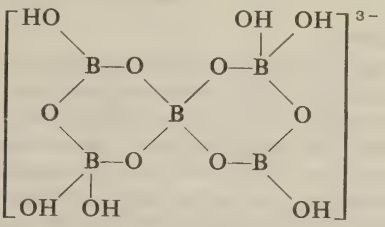
As with other borates ulexite and its products of dehydration dissolve incongruently in water[576] and equilibrium is reached slowly. This probably accounts for some disparity in the solubilities of ulexite at 25°C, recorded as being 0·23% B_2O_3[134] and 0·47% B_2O_3.[165] The solubility and rate of dissolution of ulexite in solutions of hydrochloric acid[68], nitric acid[164] and sulphuric acid have been determined.[168] The solubility in saturated gypsum solutions is less than in water at the same temperature, which gives evidence for the order of formation of ulexite and associated minerals under natural conditions.[46]

Depending on the conditions, ulexite hydrolyses in a variety of ways.[312] At temperatures between 80 and 100°C moistened ulexite loses 6 molecules of water and transforms to probertite; this conversion takes 4 weeks to complete.[22] In the presence of more water and at temperatures between 25 and 100°C a 4:5 borate with 8·5–13 molecules of water is formed. Hydrolysis of ulexite with 26 times its weight of water for some days at 40–55°C, followed by filtration of the solid and treatment with another 26 times its weight of water, produces good crystals of $2CaO,3B_2O_3,9H_2O$.[259] Hydrolysis in the presence of boric acid and meyerhofferite seed at 90°C gave the 2:3:7 borate. Hydrolysis in the presence of sodium or calcium chloride at 70°C produces colemanite ($2CaO,3B_2O_3,5H_2O$) or in saturated sodium chloride solution at 110°C produces pandermite ($4CaO,5B_2O_3,7H_2O$).[22] The dehydration of ulexite has been studied by differential thermal analysis.[141] Solid-phase reactions between ulexite and sodium carbonate have been studied, together with the solubility of the reaction products.[296, 297] A method of production of pentaborate salts from Ulexite has been patented.[593]

A review of the modern knowledge of the crystal form, density and optical properties is of special interest.[215] The X-ray pattern of ulexite is available in an indexed form.[313] Ulexite has peculiar fibre-optical properties which have been studied extensively.[314] By using ^{11}B n.m.r. techniques the boron sites in the structure have been identified and the upper and lower limits of the quadruple coupling have been found. The data confirmed the existence of the $[B_5O_6(OH)_6]^{3-}$ ion in ulexite which is related to the pentaborate ion[315]:



Pentaborate anion



Ulexite anion

This ulexite anion is also related to the $[B_5O_7(OH)_4]_n^{3n-}$ chains previously found in proberite (q.v.).[316]

Calcium Potassium Borate

$K_2O,CaO,4B_2O_3,12H_2O$. On mixing solutions of calcium chloride and potassium tetraborate ($K_2O,2B_2O_3,4H_2O$) crystals of this compound form (via an amorphous precipitate) after a few hours. The essential for good crystallization is that the pH is kept high, by using at least double the theoretical quantity of potassium tetraborate. If the stoichiometric quantities of reactants are used an amorphous calcium borate is formed. The crystals have $d_{25} = 1{\cdot}80$, and the dehydrated product has $d_{25} = 2{\cdot}36$. The solubility in water is 7·3 g/litre at 20°C. Eight molecules of water are lost after 5 days at 70°C; after 6 days at 100°C a further 1·5 molecules of water are lost; 18 days at 130°C gives a product containing 1·25 molecules of water.[317–18] Conditions for synthesis were subsequently optimized by computer technology.[643] An alternative preparative method is to ball-mill $CaO,B_2O_3,2H_2O$ with small amounts of KOH and H_3BO_3.[669] Analogous strontium and barium borates are formed.

Electrical conductivity determinations indicate decomposition to the tetraborate and further hydrolysis. The mobility of the anion in water is 38·7 mho/cm² and in 3% boric acid solution 13·8 mho/cm².[23] Treatment of the compound with isopropanol was found to extract more B_2O_3 than did similar treatment of its dehydration products.[644] The same workers also examined the action of water and of KCl and $MgCl_2$ solutions.[645]

Parameters corresponding to an orthorhombic cell have been calculated from X-ray studies.[318]

The structure of a potassium-calcium octaborate anion has been determined from infra-red spectrographic data.[577]

Calcium Rubidium and Calcium Caesium Borates

Compounds of the general formula $M_2O,M^IO,4B_2O_3,12H_2O$ have been synthesized where M = Rb or Cs and M^I = Ca,Sr.[321]

Unsynthesized Calcium Borate Minerals

Cryptomorphite, $Na_2O,3CaO,9B_2O_3,12H_2O$.
Franklandite, $Na_2O,CaO,3B_2O_3,7H_2O$.
Hilgardite, Parahilgardite, $6CaO,9B_2O_3,2CaO_2,H_2O$.
Johachidolite, $2Na_2O,CaO,4Al_2O_3,6B_2O_3,5CaF_2,5H_2O$.
Heidornite, $Ca_3Na_2[Cl(SO_4)_2B_5O_8(OH)_2]$.
Gaudefroyite, Mineral borate containing manganese and calcium.
Howlite, $4CaO,5B_2O_3,2SiO_3,5H_2O$.
Bakerite, $8CaO,5B_2O_3,6SiO_2,6H_2O$.

Other minerals containing calcium will be found in the magnesium and strontium sections.

Calcium Borates containing other Anions

Silicates

The mineral *datolite* ($2CaO,B_2O_3,2SiO_2,H_2O$) has been crystallized from alkaline borate solutions rich in calcium and carbon dioxide having a pH of 8·0–8·5 at 280–350°C. $(B_4O_7)^{2-}$ and $BSi_2O_6^-$ ions occur in the solutions.[210] The formation of a calcite film on the surface of datolite during the production of boric acid by leaching sintered datolite is the cause of considerable retention of boric oxide in the slurries.[578] Datolite and danburite were identified products from a hydrothermal study of the system $CaO–B_2O_3–SiO_2–H_2O$ at 250 and 415°C.[640] The germanium analogue of datolite was found in a similar study.[641]

Electron paramagnetic resonance data at 77 and 290 K are reported for datolite.[579]

Arsenates

The mineral *cahnite* $4CaO,B_2O_3,As_2O_5,4H_2O$ is the only example of a hydrated calcium boroarsenate. It has not been synthesized.

Borotartrates

Borotartrates exist as well defined crystalline compounds. The following calcium borotartrates are known:

	Properties
$5CaO,B_2O_3,4C_4H_4O_5,16H_2O$	$d_{25} = 1{\cdot}62$; solubility 2·46 g/l.[319]
$CaC_4H_3O_5BO_2,3H_2O$	Equilibrium constants, solubility products, heating curves.[27]
$2(NH_4)_2O,3CaO,B_2O_3,4C_4H_4O_5,10H_2O$	$d = 1{\cdot}55$; solubility 1·77 g/l[320], heating curve.

The structural formulae of these tartrates may correspond to that described for barium borotartrate (q.v.).

Boropentaerythritol

The compound was prepared from boric acid, calcium chloride, ammonium hydroxide and pentaerythritol.[646] The formula $CaO,B_2O_3,2C_5H_8O_2,9H_2O$ was assigned and supporting infra-red absorption, crystallographic and thermodynamic data were given. Aqueous solubility is 0·975 g/l at 25°C and $d = 1{\cdot}55$ g/cm^3.

STRONTIUM BORATES

Anhydrous Strontium Borates

Three corroborated anhydrous strontium borates exist in the $SrO–B_2O_3$ system. These are the 1:1, 1:2 and 2:1 borates (Mellor, V, 86); whether or not the 3:1 is a stable solid phase of the system is doubtful. In a recent study by Witzman and Beulich[322] its presence was unconfirmed. The latter study was aimed at giving information on the properties of activated strontium borates as phosphors. Other work comparing the luminescent properties of various unactivated anhydrous strontium borates[323] and those activated by manganese[324] and lead[19] has been carried out. A portion of the $SrO–B_2O_3$ (see Fig. 23) system (40–100% B_2O_3) has been studied and the phase boundaries deduced[325]; evidence for a 1:3 borate is given. Crystallographic studies[326] deducing cell dimensions and space groups and differential thermal analysis[322] have provided evidence of structures in the anhydrous system.

A number of anhydrous systems containing strontium have been studied in connection with glass formation and reference may be made to the section of this work specifically dealing with glass. The following systems have been studied and give an idea of the types of systems involved:

Li_2O–SrO–B_2O_3; plotting of fusibility diagram.[5, 327]
K_2O–SrO–B_2O_3; general glass study.[327]
Bi_2O_3–SrO–B_2O_3; general glass study.[328]
Nd_2O_3–SrO–B_2O_3; study of resulting solid phases.[329]
Ho_2O_3–SrO–B_2O_3; in relation to producing phosphors.[329]
Sm_2O_3–SrO–B_2O_3; in relation to producing phosphors.[330]
Eu_2O_3–SrO–B_2O_3; in relation to producing phosphors.[330]
Ln_2O_3–SrO–B_2O_3; in relation to producing phosphors.[330, 331]

X-Ray scattering curves of strontium borate glasses have been published.[332] Strontium borate glasses were used in an electron spin resonance study of Mn^{2+}.[603] The electrical conductivity of pure and ytterbium-activated strontium metaborate has been measured.[616]

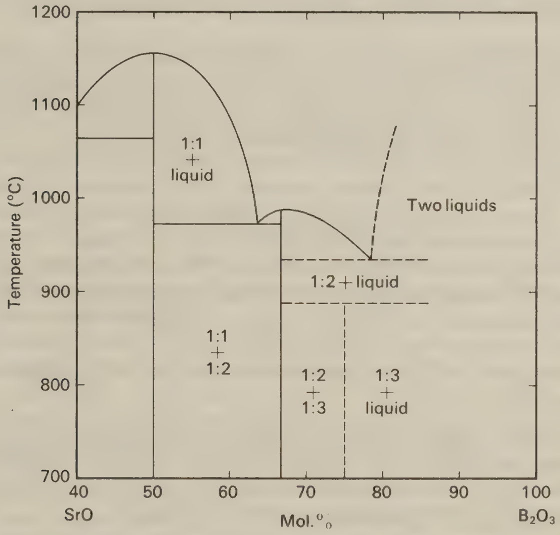
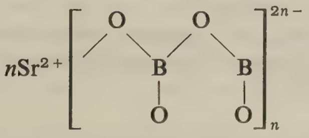


FIG. 23.—Phase equilibrium diagram for a portion of the system SrO–B_2O_3, including $SrO,3B_2O_3$[325]

SrO,B_2O_3. This compound crystallizes from a molten equimolar mixture of strontium oxide and boric oxide, or from the melt resulting from the dehydration of the tetrahydrate.[21] It is isostructural with the magnesium, calcium and barium 1:1 borates, the boron network consisting of a chain of triangularly co-ordinated boron atoms[333]:



X-Ray diffraction patterns have been published for SrO,B_2O_3[334], which has a fluorite structure. The electrical conductivity of strontium metaborate with anion excess has been studied.[582] The melting point of the dehydrated product from the 1:1:4 hydrate is 1070°C[21], slightly different from the 1100°C quoted in older references.

Refs. p. 583

Three mixed systems including SrO,B_2O_3 have been studied, with the following conclusions[7]:

(1) *MgO,B_2O_3–SrO,B_2O_3*. Compound formation at 61 and 33 mol.-% MgO,B_2O_3, with incongruent m.p. at 988 and 960°C, respectively, and a eutectic at 42·5 mol.-% MgO,B_2O_3.
(2) *CaO,B_2O_3–SrO,B_2O_3*. No compound formation—contains series of solid solutions with a minimum at 1062°C.
(3) *BaO,B_2O_3–SrO,B_2O_3*. Phases between 38·5 and 83 mol.-% indistinct, but eutectics occur at 38·5 and 83·5 mol.-%, at 1044 and 1072°C, respectively.

The anhydrous metaborate has been used as a target material in preference to elemental strontium because of its stable cyclotron operation and radiation stability, even though its efficiency in producing radioactive strontium is only 35%.[201]

$SrO,2B_2O_3$. A study of the rate of crystal growth of this compound from its melt showed that the maximum rate of growth was 9590 μm/min at 103°C of undercooling.[580] Temperature dependence of growth rate and also the viscosity of the melt were later studied.[604]

Details of single-crystal growth are quoted by the author of a paper describing an X-ray study by single-crystal methods. The lattice is orthorhombic and the pycnometric density is 3·78.[335] It is isomorphous with $PbO,2B_2O_3$.[333] More recent determination of the m.p. is not recorded (Guertler gave 930°C).

The structure of this compound is of interest because of breakdown of the rule that the number of foreign cation charges is equal to the number of borons in four-fold co-ordination. The structure was solved by a three-dimensional Fourier synthesis and proved to be a three-dimensional network of BO_4 tetrahedra in which, unusually, some oxygen atoms are bonded to three borons.[336–7] The structure could be described as a chain of triply-charged triborate ions linked along the edges and at the apices to form a three-dimensional structure.[63] X-ray diffraction data on this borate are available.[338]

Lead-activated $SrO,2B_2O_3$ has been investigated for its luminescent properties.[339]

$SrO,3B_2O_3$. There is some proof that this is a true compound. The pentahydrate dehydrates giving an anhydrous material with the formula $SrO,3B_2O_3$ which after annealing has a density of 2·78 and a melting point 925°C.[21] Further evidence for the 1:3 borate is given in a phase-diagram study[325] (Fig. 23).

$SrO,4B_2O_3$. This compound is referred to in a study of the luminescent properties of lead-activated $SrO,2B_2O_3$ and $SrO,4B_2O_3$[339]; it has also been studied when activated with samarium oxide.[340]

$2SrO,B_2O_3$. As well as appearing as a solid phase in the SrO–B_2O_3 system, with a melting point of about 1130°C, this compound also crystallizes from the obscure Sm_2O_3–SrO–B_2O_3 system.[330] Its structure has been investigated recently.[341]

The 2:1 borate is a good 'mineralizer' and has been used as an additive to 1:1 mixtures of $SrTiO_3$ and $SrZrO_3$, giving very strong non-porous enamels obtained by treating the mix at 1150°C for some time, compressing at 500 atmospheres, and then heating for 3 hours at 1450°C.[342]

$3SrO,B_2O_3$. The orthoborate is a doubtful solid phase of the SrO–B_2O_3 system but is a sufficiently well characterized borate to deduce from its infra-red spectrum that it has a dimeric arrangement of ions.[8] It has been identified, and characterized by infrared spectra, as a product from the oxidation of $Sr_3B_2N_4$ at 700°C.[675] Diffraction patterns are given. As with the 2:1 borate the orthoborate has a densifying effect in a 5% addition to $SrZrO_3$ in enamel formation.[343]

Other Anhydrous Strontium Borates

A few mixed anhydrous strontium borates have been recorded. The crystal structure of distrontium boro-aluminate, $2SrO,Al_2O_3,B_2O_3$ has been determined.[605] $Sr_2Mg(BO_3)_2$ has been synthesized and found to be a good host lattice for Tb^{3+} luminescence.[659] The rare earth system Sm_2O_3–SrO–B_2O_3 has been studied[330] at 1100°C and one of the solid phases found to be the compound $Sm_2O_3,3SrO,2B_2O_3$. Compounds of the general formula $M_2O_3,3SrO,2B_2O_3$ (where M = La, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) have also been prepared.[331, 581] Their infra-red spectra have been studied.[581] X-Ray diffraction data and space groups of praseodymium, gadolinium and lanthanum strontium borates have also been examined.[361, 615] Crystal structures of double borates of strontium with lanthanum[611], neodymium[612] and praseodymium[613–14] have been determined. Solubilities and phase equilibria in the anhydrous systems SrO–Ln_2O_3–B_2O_3 have been measured (Ln = Nd[617], Ho[617], Sm[618] and Eu.[618] In group IV a tin compound is formed, isostructural with dolomite[10], formulate as SnO_2,SrO,B_2O_3.[9, 344] Both a phosphate and an arsenate are formed, the former by heating strontium carbonate, diammonium phosphate and boric acid together, and the latter by the reaction of strontium carbonate, arsenic acid and boric acid at high temperatures. The arsenate is isotypical with the corresponding calcium compound. Both compounds melt incongruently and are stable to methyl alcohol, but decomposed by water and dilute acids.[129] In parallel with the other alkaline earths, strontium forms a compound of the formula $Sr[B(SO_4)_2]_2$, prepared by the reaction of strontium sulphate with boric acid and sulphur trioxide. The compound is very hygroscopic and is ionic in character.[11] Halogenoborates of the general formula $3MO,5B_2O_3,MX_2$ have also been found.[373]

Hydrated Strontium Borates

Compared with magnesium and calcium compounds the hydrated borates of strontium have had little attention, in part owing to the rarity of industrially exploitable strontium borate minerals.

A systematic investigation of the SrO–B_2O_3–H_2O system was not performed until Lehmann et al. studied it at 0, 30, 100 and 190°C.[345, 346] Previous to that Gode et al. had outlined the Na_2O–SrO–B_2O_3–H_2O system.[347] Parkerson, who has carried out a variety of hydrothermal syntheses of alkaline-earth borates, has also studied the formation of strontium borates in the following reactions[348]:

(a) Borax with strontium iodate.
(b) Conversion reactions of strontium borates in borax/boric acid mixtures.
(c) Ammonium pentaborate with strontium nitrate.
(d) Ammonium pentaborate with strontium iodate.

Debye-Scherrer X-ray patterns of various strontium borate hydrates have been determined.[346] Infra-red spectra of aqueous strontium borates have been studied.[649]

SrO,B_2O_3,H_2O. The monohydrate is reported to be formed from an aqueous solution ($\geqslant 10$M) of strontium hydroxide and boric acid maintained at 190°C for some hours; it was characterized by X-ray.[346]

$SrO,B_2O_3,2H_2O$. Apart from being a dehydration product of the 1:1:4 strontium borate[21], no further work on this rather doubtful compound has been carried out since Ouvrard claimed to produce it from the action of water on anhydrous SrO,B_2O_3.

$SrO,B_2O_3,4H_2O$. This is the best characterized of all the hydrated strontium borates. It is found in the SrO–B_2O_3–H_2O system between 0 and 100°C.[346] It is also formed by treating a sodium borate solution with strontium nitrate[347] or strontium chloride.[267] Care must be taken to adjust the $Na_2O:B_2O_3$ ratio so that the pH throughout the reaction is 11·4–12·0. Crystal formation takes place after about 30 minutes at 60°C or several hours at room temperature. It is important to exclude carbon dioxide from the reaction mixture. A further two methods of formation have also been described.[348]

The tetrahydrate usually crystallizes in two forms, monoclinic and triclinic, with densities 2·56 and 2·55, respectively.[97] Elsewhere the density of the product is variously quoted as 2·58[349] and 2·59.[21] The thermograms of both modifications are the same.[350] Both monoclinic and triclinic forms have been shown to have boron atoms tetrahedrally co-ordinated by four oxygen atoms.[250] Both forms have had their unit-cell dimensions determined.[351] The monoclinic is isomorphous with the corresponding barium borate, $Ba[B(OH)_4]_2$.[349, 352-3] There are eight formula units to a cell, and no direct linkage of $B(OH)_4$ groups, each of which is co-ordinated with three strontium atoms. The strontium sites have been deduced from multiple-film Weissenberg photographs.[354] The triclinic modification has also had its structure deduced.[355]

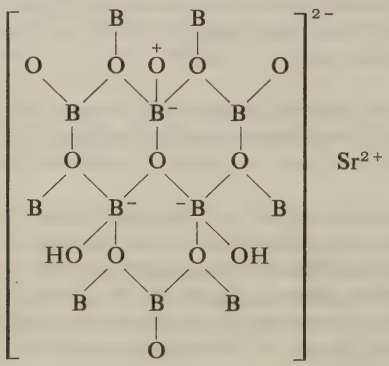
Investigations into the electrical conductivities and cryoscopic properties of the compound during hydrolysis by water indicate the complete breakdown to the Sr^{2+} ion and boric acid.[23] The solubility at 20°C is 0·014 mol SrO and 0·018 mol B_2O_3 per litre of water after 2 days, and 0·016 and 0·032 mol after 16 days.[21] The compound is soluble in excess of strontium chloride solution, probably owing to complex formation.[356]

After 10 days' heating at 100°C a fine powder which does not pick up water at room temperature is formed; the powder corresponds to a 1:1:2 borate. Further heating for 1 day at 130°C produces the 'monohydrate' and at 180°C the remaining water is lost slowly.[21]

$SrO,2B_2O_3,4H_2O$. No confirmation of the existence of this compound has been forthcoming since Ditte reported producing it by double decompositions between borax and strontium chloride (Mellor, V, 92).

$SrO,3B_2O_3,4H_2O$. Until 1963 this compound was known only as the mineral *tunnelite* (q.v.) when it was synthesized together with three other hydrated strontium borates by studying the reaction of ammonium pentaborate with strontium chloride and strontium iodate.[348] Other attempts have been made to synthesize tunnelite.[311]

The crystals of tunnelite belong to the monoclinic system and are isostructural with nobleite ($CaO,3B_2O_3,4H_2O$). X-Ray studies showed that structurally it consisted of sheets of borate polyions, held together by hydrogen bonding through the associated water molecules[357], and Sr^{2+} ions. Each of the metallic ions is co-ordinated with 10 oxygen atoms.[358] By studying the quadrupolar splitting of ^{11}B n.m.r. signals in a single crystal, all the boron sites were determined. Three borons were found to be tetrahedrally co-ordinated and 3 triangularly, and of special interest was the fact that the former 3 atoms were all bonded to 1 oxygen atom.[359] Thus a fused-ring structure was postulated with a formula best represented as $Sr[B_6O_8(OH)_2],3H_2O$, and the unit cell content roughly given by:



$SrO,3B_2O_3,H_2O$. This has been given as the formula for *para-veatchite*, which is now regarded as $3SrO,8B_2O_3,5H_2O$ (q.v.).

$SrO,3B_2O_3,2H_2O$. The mineral *veatchite* is chemically $SrO,3B_2O_3,2H_2O$.[360] The hydrothermal reaction of strontia and boric acid or tunnelite and boric acid at 260°C gives a compound of the same formula as veatchite with a density of 2·77.[265] Less certainly, because of side reactions, it is reported as being formed by hydrothermal conversion of the 1:3:5 compound in a sealed vessel.[345]

The formula of veatchite belongs to the order of chain borates, but it is uncertain whether the anion is a single ring, $[B_3O_4(OH)_2]^-$ or has a dimeric form, $[B_6O_7(OH)_6]^{2-}$.[360]

$SrO,3B_2O_3,5H_2O$. This compound is found in the system $SrO–B_2O_3–H_2O$ within the temperature range 0–100°C.[346] It may also be synthesized by mixing a soluble strontium salt with a sodium borate solution of $Na_2O:B_2O_3$ ratio 2:7, in such a way that $\frac{5}{7}$ of the boric oxide is left in the solution after precipitation. It takes 3 days for crystalline spherules of the compound ($d_{25}=2{\cdot}18$) to form from the amorphous precipitate. Its formation from strontium acetate and boric acid after heating a 1:6 molar ratio mixture below the boiling point for several days is also described.[21] The strontium analogue of ulexite ($Na_2O,2SrO,5B_2O_3,16H_2O$) on standing in a 3% boric acid solution transforms into $SrO,3B_2O_3,5H_2O$.[363]

Hydrolysis of the compound occurs, at first with more strontium oxide dissolving than corresponds to a solution of $SrO,3B_2O_3$; after 2–3 days the strontium oxide content of the water decreases (0·014 mol → 0·005 mol) and eventually after 70 days the $B_2O_3:SrO$ ratio is 10·0.[21] The mobility of the ions in 3% boric acid solution has been measured, showing no hydrolysis.[23]

The compound dehydrates in the following manner[21]:

at 50°	$4H_2O$ remain
100°	$3H_2O$ remain
140°	$2H_2O$ remain
200°	$1H_2O$ remains
450°	last traces lost
925°	m.p.

Another author formed the anhydrous 1:3 compound by heating the pentahydrate at 820°C for several hours; in this case it was found to be stable up to 975°C, at which it melted.[364]

The structure of this compound has not yet been investigated, but has been characterized by X-ray analysis, and powder X-ray data given.[346]

$SrO,4B_2O_3,2H_2O$. This compound is found in the $SrO–B_2O_3–H_2O$ system at 190°C and has been characterized by X-ray analysis.[346]

The structure suggested is $Sr[B_8O_{12}(OH)_2],H_2O$[365], which is postulated as belonging to the order of 'sheet borates with mixed polyions'.[63] Later work assigns the structure as $Sr[B_8O_{11}(OH)_4]$ and claims the anion to be a new radical.[671]

The 7 and 12 hydrates of the 1:4 strontium borates have not been confirmed.

$2SrO,B_2O_3,5H_2O$. The only reference to this compound is that it is formed by the prolonged contact (over weeks) of the strontium analogue of ulexite ($Na_2O,2SrO,5B_2O_3,16H_2O$) with water.[363]

$2SrO,3B_2O_3,5H_2O$, etc. This, the analogue of colemanite, was synthesized recently[348] from solutions free from foreign ions, via intermediate polyborate ions.[345] It has ferroelectric properties like colemanite ($2CaO,3B_2O_3,5H_2O$) and is isomorphous with it.[348] The hexahydrate ($2SrO,3B_2O_3,6H_2O$) is reported to be formed in the $SrO–B_2O_3–H_2O$ system at 100°C. An amorphous borate corresponding to $2SrO,3B_2O_3,9H_2O$, formed at 30°C, is also described.[346] The hexahydrate was characterized by X-ray analysis.

$3SrO,8B_2O_3,5H_2O$. A compound corresponding to the above formula was found in the $SrO–B_2O_3–H_2O$ system at 190°C.[346] It was suggested that this compound was identical with veatchite ($SrO,3B_2O_3,2H_2O$), but the known cell volume could not accommodate this formula.[366] More recently it has been suggested that it was identical with the mineral para-veatchite (which can have some calcium substituted for the strontium), and an X-ray study implied a formula

$$Sr_3[B_3O_4(OH)_2]_2[B_5O_8(OH)]_2,2H_2O \qquad \text{(ref. 367)}$$

However, the author of the latter work had, in an earlier paper, proposed from chemical analyses a formula $4SrO,11B_2O_3,7H_2O$, which, if the unit cell was written $2[(Sr,Ca)_2B_{11}O_{18}(OH),3H_2O]$, agreed well with the crystal lattice parameters and the density of 2·685.[368] In 1968 another worker partly corroborated this latter work by an X-ray study, deducing that the formula of the monoclinic cell of para-veatchite was $Sr_2[B_5O_8(OH)]_2B(OH)_3,H_2O$[369], i.e. $4SrO,11B_2O_3,7H_2O$. It is obvious that some confusion still exists; it does not yet seem certain that the synthetic 3:8:5 borate is identical with para-veatchite and the synthetic 3:8:5 borate could possibly be formulated as the 4:11:7 borate. As can be seen by the comparison of analytical values below it is very difficult to distinguish between the two alternatives chemically; full structural analysis would perhaps provide a solution.

	$3SrO,8B_2O_3,5H_2O$ (theory)	$4SrO,11B_2O_3,7H_2O$ (theory)
SrO	32·5%	31·7%
B_2O_3	58·2%	58·6%
H_2O	9·3%	9·7%

Hydrated Strontium Double Borates

Strontium Sodium Borate

The strontium analogue of ulexite, $Na_2O,2SrO,5B_2O_3,16H_2O$, is prepared as needle-like crystals ($d_{25} = 2{\cdot}06$) by mixing 20 ml of water containing 0·01 mole of $SrCl_2,6H_2O$ with a solution of 0·015 mole of $Na_2O,2B_2O_3,10H_2O$ and 0·005 mole of sodium hydroxide in 80 ml of water, and allowing it to stand for a week. $2SrO,B_2O_3,$-$5H_2O$ (q.v.) is formed from strontium 'ulexite' by standing in water for many weeks. In contact with a 3% boric acid solution it is transformed into $SrO,3B_2O_3,$-$5H_2O$ (q.v.). Two mols of water are lost by heating at 64°C, and further loss occurs between 64 and 120°C until the tetrahydrate is left, which appears stable between 120 and 150°C. The remaining water is lost in two stages: two mols at 150–190°C and the last two at 250–320°C.[363] A similar composition made from borax, strontium nitrate and sodium hydroxide was assigned the formula $NaSr[B_5O_6(OH)_6],5H_2O$.[609] It dehydrated at 100–205°C and an exothermic effect at 755°C assumed to correspond to a structural rearrangement.

Strontium Potassium Borate

$K_2O,SrO,4B_2O_3,14H_2O$ is prepared in the same way as the corresponding calcium salt (q.v.), strontium chloride being used in place of calcium chloride. It has similar properties to those of the calcium salt.[21]

Strontium Rubidium and Strontium Caesium Borates

Compounds corresponding to the formula $M_2O,SrO,4B_2O_3,12H_2O$ (M = Rb and/or Cs) have been synthesized.[321]

Strontium Calcium and Strontium Magnesium Borates

In the mineral field the following have indeterminate substitution of calcium for strontium and *vice versa*:

Kurgantaite	$(Ca,Sr)_2[B_4O_7(OH)_2]$
Strontio-hilgardite	$Ca_{1\cdot08}Sr_{0\cdot92}[B_5O_8(OH)_2Cl]$
Strontio-borite	$4(Ca,Sr)O,2MgO,12B_2O_3,9H_2O$
Strontio-ginorite	$(Sr,Ca)_2B_{14}O_{23},H_2O$

During a study of the simultaneous crystallization of calcium and strontium diborates at 25°C, solid solutions were obtained from solutions containing an excess of Sr (> 50%).[648]

Strontium Borates Containing Other Anions

Trihydroxy Glutarates

The following three salts have been formed by the reaction of various proportions of strontium nitrate with boric acid and trihydroxyglutaric acid in aqueous ammonical medium.[370]

$$2SrO,3(NH_4)_2O,B_2O_3,3C_5H_6O_6,12H_2O;$$
$$3SrO,2(NH_4)_2O,B_2O_3,3C_5H_6O_6,16H_2O;$$
$$3SrO,B_2O_3,3C_5H_6O_6,12H_2O.$$

Thermograms of these compounds are quoted.

Borotartrates

A strontium borotartrate of the form $SrC_4H_3O_5BO_2,2H_2O$ has been synthesized, together with other alkali and alkaline-earth borotartrates. The equilibrium constants and solubility products of the products are given.[27]

An ammonium strontium borotartrate is also known; it has a density of 1·95 at 25°C, a solubility of 1·83 g/l at 20°C and is formulated $2(NH_4)_2O,3SrO,B_2O_3,4C_4H_4O_5,10H_2O$.[320]

The structural formulae of these borotartrates are probably analogous to that suggested for barium borotartrates (q.v.).

BARIUM BORATES

Anhydrous Borates

Guertler's original investigation of the $BaO–B_2O_3$ system extended only between 40 and 80 mol.-% BaO because of difficulties in crystallization (Mellor, V, 86). However, de Carli included the range 0–40 mol.-% BaO, establishing the existence of the 1:2 and 1:4 barium borates and the possibility of a 1:3 borate.[371] Later Levin and McMurdie, using the quenching method of system investigation, derived a phase equilibrium diagram[372], demonstrating the presence of the 1:4, 1:2, 1:1 and 3:1 compounds with congruent melting points. The latter workers also showed that there is a region of liquid immiscibility extending from 1·6–30·2 mol.-% BaO and from 868 to above 1500°C[372] (cf. $CaO–B_2O_3$ and $SrO–B_2O_3$ systems). The range of immiscibility was modified by Levin later (see Fig. 24[207]). The crystal-optic properties of the anhydrous borates have been studied.[326]

By the addition of foreign ions the area of immiscibility may be reduced or removed. Ions investigated were those of alkalis and alkaline-earths, Pb^{2+}, Cd^{2+} and Al^{3+}.[2] By the addition of 3% of K_2O to the system it was possible to prevent two-layer separation, and surface tensions at various compositions could be plotted.[181] By using the same technique the calcium, strontium and barium borate systems were investigated, and the viscosity, density and electrical resistance of various melts were determined.[3] Without homogenization it was shown that the surface tension of the top layer of the immiscible system was the same as that of molten boric oxide. The surface tension rose rapidly with increasing BaO concentration in the homogeneous part of the system.[1] The viscosity at temperatures between 850 and 950°C showed a maximum at about 22–23 mol.-% BaO. The specific and equivalent conductivities in the alkaline-earth borate melts were in the order Ba > Sr > Ca[1], and could be represented by the usual formula $\log_e$ (specific conductivity) $= -(A/T)+B$; A was twice that for the alkali-borate glasses and increased as the BaO content increased.[374] A similar increase was found in the $NaO–BaO–B_2O_3$ system.

The coefficients of expansion and deformation temperatures throughout the

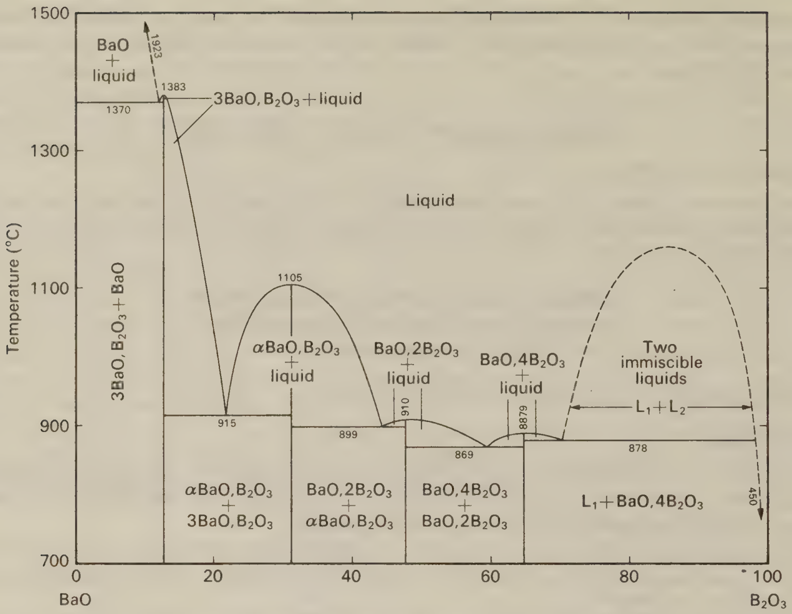


FIG. 24.—Phase diagram of the system BaO–B_2O_3[372]

BaO–B_2O_3 system have been studied.[375] In an investigation of BaO/B_2O_3 mixtures for glass electrodes they were shown to be unsuitable above 46·9% BaO because of their hygroscopicity, and below 47%, because they gave no dependable results.[376] The heat of devitrification in the BaO–B_2O_3 system showed a minimum at 20 mol.-% BaO. The oxygen availability has a minimum at the same point on the composite curve.[377] X-Ray scattering curves of barium borate glasses have been compared with those of strontium borate glasses.[332] Glass formation is possible in the BaO–B_2O_3 system if the cooling rate is high.[378]

Recent ^{11}B n.m.r. spectrum work on the BaO–B_2O_3 system and its crystalline phases shows the presence of BO_3 (planar) and BO_4 (tetrahedral) groups. At about 33 mol.-% BaO, dipole second moments, line widths and coupling constants all agreed with four co-ordinated borons throughout.[379–81]

Various ternary and quaternary systems containing barium and boric oxides have been studied mainly in the search for glasses of particular properties:

Li_2O–BaO–B_2O_3	*d,n*, chemical stability and thermal expansion determined. (ref. 5)
MgO–BaO–B_2O_3 TiO_2–BaO–B_2O_3	Cooling of glasses studied. (ref. 57)
TiO_2–BaO–B_2O_3	Effect of time and temperature on devitrification studied. (ref. 382)
SiO_2–BaO–B_2O_3	Immiscibility volume calc. (ref. 383)
SiO_2–BaO–B_2O_3	Extensive study—new compound $3BaO,3B_2O_3,SiO_2$ found. (ref. 384) (see Fig. 25)
Al_2O_3–BaO–B_2O_3	System study. (ref. 586)
Bi_2O_3–BaO–B_2O_3	Structure study, role of B^{3+} ion in glass formation. (ref. 328)
Fe_2O_3–BaO–B_2O_3	Studies of magnetic microcrystalline materials produced by crystallization of glasses in system. (refs. 385–7)
Li_2O–SiO_2–BaO–B_2O_3	Rate of crystal growth. (ref. 388)
($50PbO+50B_2O_3$)–$PbTiO_3$–$Ba(BO_2)_2$–$BaTiO_3$	No borate crystals formed. (ref. 389)
$YTaO_4$–BaO–B_2O_3	Phase equilibrium and crystal growth. (ref. 585)

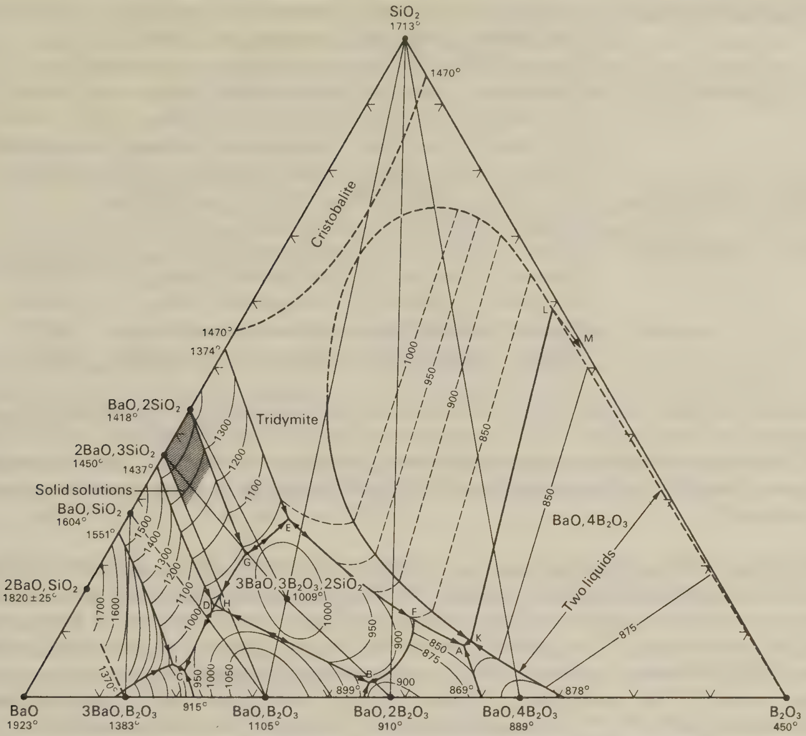


FIG. 25.—Phase diagram for the system $BaO–B_2O_3–SiO_2$[384]

A—810 ± 10°C
B—875 ± 5
C—875 ± 5
D—920 ± 10
E—950 ± 20

F—825 ± 10°C
G—980 ± 5
H—925 ± 10
I—962 ± 10
J—< 1370

K—815 ± 10°C
L—815 ± 10
M—< 450

Barium borates have been extensively investigated as white pigments with fungicidal properties.[390–2]

The solubility of copper in a 42:58 $BaO:B_2O_3$ melt was 0·08%; it was 0·097–0·1% in a 32:68 $BaO:B_2O_3$ melt.[393]

The crystallization of nickel ferrite ($NiFe_2O_4$) from barium borate fluxes has been studied in detail especially in the 1100–1300°C temperature range.[583–4]

BaO,B_2O_3. This compound crystallizes from the $BaO–B_2O_3$ system[371] as a compound melting at 1105°C[384] (see Fig. 22). The formation of the compound activated with a small percentage of lead has been described and its properties as a phosphor discussed.[17]

It has been shown that there are two polymorphs of barium metaborate, of which only the high-temperature form has been investigated structurally.[333] A new low-temperature modification was made by dehydrating the recently discovered $BaO,B_2O_3,1\frac{2}{3}H_2O$ at 300°C.[394] The infra-red spectrum of a powder sample changes as the compound ages, owing probably to the degree and type of polymerization.[8] The optical properties and X-ray diffraction patterns have been recorded[372], and the structure shown to belong to the system of non-ring chain borates, as with the analogous lithium and other alkaline-earth borates.[333] Modifications of the structure have been published.[395] The compound activated with samarium shows line spectra characteristic of the fluorite structure.[14]

The reaction of barium metaborate with magnesium, calcium, strontium and cadmium metaborates gave the following indications of compound formation etc.[7]

MgO,B_2O_3–BaO,B_2O_3	50 mole-% BaO,B_2O_3, compound, incong. m.p., 1010°C. $\sim$30 mole-% BaO,B_2O_3, eutectic pt., 950°C. 68 mole-% BaO,B_2O_3, polymorphic transformation.
CaO,B_2O_3–BaO,B_2O_3	22·5 mole-% CaO,B_2O_3, compound, cong. m.p., 1056°C. 42 mole-% CaO,B_2O_3, compound, incong. m.p., 1060°C. 53·5 mole-% CaO,B_2O_3, compound, incong. m.p., 1080°C. 67 mole-% CaO,B_2O_3, compound, incong. m.p., 1074°C.
SrO,B_2O_3–BaO,B_2O_3	38·5 mole-% BaO,B_2O_3, eutectic pt., 1044°C. 83 mole-% BaO,B_2O_3, eutectic pt., 1072°C.
CdO,B_2O_3–BaO,B_2O_3	30 mole-% BaO,B_2O_3, compound, incong. m.p., 870°C. 82 mole-% BaO,B_2O_3, compound, incong. m.p., 1000°C. 58·5 mole-% BaO,B_2O_3, compound, cong. m.p., 1018°C. 17 mole-% BaO,B_2O_3, compound, eutectic pt., 790°C. 70 mole-% BaO,B_2O_3, compound, eutectic pt., 950°C.

Barium metaborate has been patented widely as a mould-resistant pigment for incorporation into paints[390–2, 667]; a number of articles have appeared on the subject.[397–9] It has been used in preference to metallic barium, with a 40% loss of efficiency but greater stability, in the production of radioactive barium by using it as the target in a cyclotron.[201]

$BaO,2B_2O_3$. Monoclinic crystals, isomorphous with $SrO,2B_2O_3$ and $PbO,2B_2O_3$, crystallize from the BaO–B_2O_3 system[371–2] and have a melting point of 910°C.[384] The growth rates of both $BaO,2B_2O_3$ and $PbO,2B_2O_3$ were measured at various degrees of undercooling. The growth rate of the barium compound was found to be higher.[602] This anomaly was explained by proposing a chain-folding mechanism for crystal growth.[587] The structure has been thoroughly investigated by means of powder X-ray techniques[312, 333, 400], three-dimensional Patterson and electron-density syntheses[555], and ^{11}B n.m.r. spectrum determinations.[380] A three-dimensional lattice of alternating single and double rings is postulated. Each of the rings in the double structure has two tetrahedral boron atoms, one of which is common to both rings. The single rings contain only triangular boron atoms. Each single ring is linked only to double rings, and vice versa. The barium atoms fit into the channels of this network.[400] The compound is best represented as $Ba_2[B_8O_{14}]$. Like the 1:1 borate, the 1:2 borate has been used as a pigment in mould-resistant paints.[390]

$BaO,4B_2O_3$. As well as appearing as a solid phase in the BaO–B_2O_3 system[371–2], this compound is also a primary solid phase in the BaO–SiO–B_2O_3 system.[384] It crystallizes from the melt formed by heating one part of barium carbonate with eight of boric acid at 1000°C.[401] When the same mixture, to which 25 mole-% of V_2O_5 has been added, is used at 1250°C, the 1:4 borate that crystallizes takes on semiconductor properties.[402]

The compound melts at 889°C[384] (other sources quote 800°C[401]). Its density is 2·91.[401]

X-Ray diffraction data are on record[372, 401], and ^{11}B n.m.r. spectra has here provided some knowledge of the tetrahedrally co-ordinated boron centres.[380] Further structural investigations[403] indicated that the structure was comparable to that of the 1:2 borate ($Ba_2[B_8O_{14}]$) in that it belongs to the order of three-dimensional borates with mixed anions[63] and may be represented as $Ba[B_8O_{13}]$. The structure of the glassy 1:4 borate has been studied by X-ray diffraction, which shows that each boron atom is tetra-co-ordinated by oxygen and the tetrahedra share edges with a distorted barium cube.[404]

Like the other anhydrous barium borates, the 1:4 borate has been patented as a mould-resistant pigment.[390] The borate activated with Eu^{2+} is an efficient phosphor.

$3BaO,B_2O_3$. The orthoborate has the highest melting-point of the anhydrous barium borates (1383 ± 5°C) and is found as a solid phase in the BaO–B_2O_3 system.[372]

Optical data and X-ray diffraction details have been obtained, and some attempt at determining the structure has been made by studying the infra-red spectrum.[8, 73]

On adding the compound to barium zirconate refractories, their porosity is reduced.[343] The orthoborate has also been used as a mould-resistant pigment.[390]

Other Binary Borates

There are slight inflections in the melting-point curve[371] of the $BaO–B_2O_3$ system at points representing the 1:3 and 2:1 compositions, indicating the possibility of compounds with incongruent melting points. The borates $2BaO,5B_2O_3$, $2BaO,B_2O_3$ and $4BaO,B_2O_3$ have been reported.[601]

Anhydrous Borates Containing Barium and Other Elements

Beryllium and Zinc. The existence of BeO,BaO,B_2O_3 and ZnO,BaO,B_2O_3 is recorded. On activation with lead they show an increase in ultra-violet emission, which increases with lead concentration.[405]

Magnesium and Calcium. $Ba_2Mg(BO_3)_2$, which is hexagonal and isomorphous with the mineral buetschliite, and $Ba_2Ca(BO_3)_2$ have been synthesized and found to be good host lattices for Tb^{3+} luminescence.[659]

Silicon. A study of the $BaO–SiO_2–B_2O_3$ system revealed the existence of a solid phase of well-defined crystalline form having the formula $3BaO,2SiO_2,3B_2O_3$.[384] The compound has been described optically and X-ray patterns recorded. It melts at 1009°C.

A compound $3BaO,SiO_2,3B_2O_3$ is quoted as having mould-resistant properties and suitable as a paint pigment.[390]

Lanthanum. The X-ray diffraction data and space-group of lanthanum barium borate have been studied.[361]

Yttrium. The compound $Y_2O_3,4BaO,B_2O_3$ is formed when a $BaO–B_2O_3$ mixture is used as a flux in the crystallization of yttrium ferrite.[607]

Titanium, Tin, Zirconium. Compounds of the general formula BaO,MO_2,B_2O_3 (where $M = Ti$, Sn and Zr) have been prepared by sintering barium carbonate, boric acid and the appropriate metal oxide at temperatures in the region of 1000°C.[9, 344, 406] The tin and titanium compounds have the dolomite structure[9, 10] and it is likely that the analogous zirconium compound is isomorphous. The stability of the former compounds has been investigated[9] and the zirconium compound has been suggested as a pigment for emulsion paints. It has a unique X-ray pattern.[406]

Sulphur. $Ba[B(SO_4)_2]_2$ has been prepared by the reaction of barium sulphate (1 mole) boric acid (2 moles) and sulphur trioxide (6 moles); with less boric acid the tri-sulphato-borate $Ba[B_3O(SO_4)_3]$ is formed. These compounds are very hygroscopic, colourless, and probably ionic with high-polymeric anions.[11]

Tungsten. The borotungstate of barium is produced by treating $Na_5H_4[B(W_2O_7)_6]$ (formed by reacting boric acid and sodium tungstate, Na_2WO_4) with barium carbonate. The barium salt is a good starting point for the production of other metal borotungstates.[407]

Halogens. A study of the system $BaF_2–B_2O_3$ and $LiF–B_2O_3–BaF_2$ showed that no ternary compounds were formed in the second system but that the following compounds existed in both systems[408]: $3BaF_2,B_2O_3$; $2BaF_2,3B_2O_3$; $BaF_2,4B_2O_3$. Halogenoborates of the general formula $3MO,5B_2O_3,MX_2$ ($M = Ba$ or Ca, Sr, Eu, Pb; $X = Cl$, Br) have been formed.[373]

Hydrated Barium Borates

The $BaO–B_2O_3–H_2O$ system has received little attention since Sborgi investigated it[409],* probably because there are no known barium borate minerals and because the anhydrous barium borates are commercially of greater interest. The majority of the work on hydrated barium borates has been performed in Russia, but recently a partial study of the $BaO–B_2O_3–H_2O$ system at boiling point by Lehmann et al. has shown the existence of a new hydrate of barium 1:1 borate, $BaO,B_2O_3,1\frac{2}{3}H_2O$.[394] Most recently, other Russian workers have identified $Ba_2B_6O_{11}$,-$6H_2O$,BaB_4O_7,$4H_2O$ and BaB_6O_{10},$4H_2O$.[608]

Good Liesegang phenomena are obtained from peptized barium borates.[237] Infrared spectra of aqueous barium borates have been studied.[649]

$BaO,B_2O_3,1\frac{2}{3}H_2O$. If precipitation is carried out at pH 11·4 or above and with the B:Ba ratio 2 or less, the aqueous mixture being kept at boiling point, a new hydrate of this formulation is obtained. The compound dehydrates at 300°C to give an interesting low-temperature form of BaO,B_2O_3 in which boron atoms are triangularly and tetrahedrally co-ordinated.[394]

$BaO,B_2O_3,4H_2O$. Small monoclinic crystals of this compound are obtained by stirring for a few hours the flaky precipitate formed by the addition of barium chloride to a sodium metaborate solution. In practice it is preferable to make the sodium metaborate solution from sodium hydroxide (de-carbonated) and borax, the reaction being carried out in 0·25M solution. The pH should be above 11.[21,410]

$$\begin{array}{llll} BaCl_2 + & Na_2B_4O_7 + & 2NaOH + 3H_2O & = BaO,B_2O,4H_2O + Na_2B_2O_4 + 2NaCl. \\ (0{\cdot}25\text{M}) & (0{\cdot}25\text{M}) & (0{\cdot}5\text{M}) & \end{array}$$

c.f. calcium and strontium metaborates. If the solutions are less concentrated (0·1M) the pentahydrate forms. The tetrahydrate can, however, form at higher temperatures at these lower concentrations.[411]

The compound dissolves in water with slight hydrolysis, giving a $BaO:B_2O_3$ ratio of 1·09 and a pH of 10·2. A saturated solution contains 13·5 g of the tetrahydrate per litre of solution at 25°. The density of the solid is 2·88.[21]

The tetrahydrate is isomorphous with the analogous strontium compound[349] having very similar optical constants.[352] Later determinations of the structure showed that the boron atoms are situated in isolated tetrahedra whose vertices are occupied by OH groups. The barium atoms are arranged in a face-centred trigonal prism and prism pairs are connected with common $B(OH)_4$ tetrahedra. The average chemical formula is $Ba[B(OH)_4]_2$.[412] Other work on the structure has not basically altered the above description.[413–14]

$BaO,B_2O_3,5H_2O$. The pentahydrate is formed in the same manner as the tetrahydrate (*q.v.*) except that it is necessary for the reactants to be more dilute and for the concentration of the hydroxide to be increased.[411]

$$\begin{array}{llll} BaCl_2 + & Na_2B_4O_7 + & 2NaOH + 4H_2O & = BaO,B_2O_3,5H_2O + Na_2B_2O_4 + 2NaCl \\ (0{\cdot}1\text{M}) & (0{\cdot}1\text{M}) & (0{\cdot}5\text{–}1{\cdot}0\text{M}) & \end{array}$$

The most recent value for the density of the monoclinic double-edged prisms of the pentahydrate is 2·79[415]; an earlier reference[21] gives a density of 2·50.

The structure of the pentahydrate has been suggested (from various data) to be $BaB_2(OH)_2O_3,4H_2O$ with the presence of both triangularly and tetrahedrally co-ordinated boron atoms.[416] Earlier[417] and later[415,418] evidence showed that the borons were all tetrahedrally co-ordinated, giving a formula closely related to that of the tetrahydrate, $Ba[B(OH)_4]_2,H_2O$.

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* It should be noted that errors exist in the references to this system in Mellor, V, pp. 86, 87; Fig. 26 on p. 86 refers to the system $CaO–B_2O_3–H_2O$, not to $BaO–B_2O_3–H_2O$ as printed. Further, Fig. 27 on p. 87 refers to $BaO–B_2O_3–H_2O$, not to the system with CaO.

$BaO,2B_2O_3,4H_2O$. Fine, roundish grains of this compound have been prepared.[608]

$BaO,3B_2O_3,xH_2O$. If the amorphous 1:2 hydrate is allowed to react with a boric acid solution an amorphous 1:3:x borate is formed slowly. This reaction can be speeded up by slight warming and agitation. The product obtained in this way has $x=6$ and is amorphous.[21, 419] A tetrahydrate is also known.[608]

The formation of crystalline 1:3 borates is accomplished by adding small portions of solid boric acid to a 10% barium acetate solution. At room temperatures slight reaction occurs, producing a crystalline compound with $x=5$; this is also obtained in preference to the tetrahydrate if the solutions are dilute.[419] By heating the mixture to 80°C and continually stirring, the tetrahydrate is formed as transparent hexagonal crystals.[21] More recently the crystalline tetrahydrate has been formed by the action of barium hydroxide on concentrated boric acid solutions at high temperatures.[421] For a product prepared in the latter manner the density is reported to be 2·30, but for a product prepared by the acetate route the density is given as 2·60. The pentahydrate has a density of 2·52, and the amorphous hexahydrate a density of 2·07.[21]

The amorphous hexahydrate is formed from the reaction between potassium 1:2 borate and barium chloride if the molar ratio is less than 4, or the concentration of the former is less than 0·2–0·3M[22]; otherwise the well-defined crystalline $K_2O,BaO,4B_2O_3,14H_2O$ is formed.[422]

Both the pentahydrate and the amorphous hexahydrate dehydrate at room temperature to the tetrahydrate, which is stable up to 50°C. It then loses 2 molecules of water between 50 and 150°C, giving a hygroscopic compound. Further heating between 200 and 300°C causes the loss of another molecule of water. Heating to 600°C is necessary before the anhydrous compound is formed.[21] Thermograms of the tetrahydrate have been determined.[608]

The water solubility of the 1:3 barium borates is very slight, but it is increased by the presence of boric acid.[23]

$2BaO,3B_2O_3,6H_2O$. This material has been prepared as an amorphous powder.[608]

Other Hydrated Binary Barium Borates

No recent evidence for the 1:4:12, 2:3:7 or 3:5:6 borates has been recorded. It is unlikely that these are anything but mixtures or amorphous compounds. A compound for the formula $Ba[B_8O_{12}(OH)_2],H_2O$ has been reported and its structure investigated.[365]

Hydrated Barium Borates Containing Other Elements

Potassium. If a solution (0·3M or more) of potassium tetraborate ($K_2O,2B_2O_3,4H_2O$) is treated with barium chloride solution so that the molar ratio $K_2B_4O_7:BaCl_2$ is greater than 5:1, rhombic platelets of $K_2O,BaO,4B_2O_3,14H_2O$ are formed, encouraged by seeding. If the conditions of formation indicated are not adhered to, the amorphous 1:3:6 borate (*q.v.*) is formed. The compound hydrolyses in water giving the amorphous $BaO,2B_2O_3,xH_2O$.[23] The formation of this barium salt is comparable with that of the analogous calcium or strontium salt (*q.v.*). The compound has a density of 2·027 and an orthorhombic unit cell.[318]

Barium is less prone to double-borate formation that the other alkaline earths. There are no ammonium barium borates.[21]

Silicon. Ready formation of barium silicates, borates and borosilicates was observed during a hydrothermal study of the $BaO–B_2O_3–SiO_2–H_2O$ system at 250 and 415°C.[606]

Tartrates. Alkaline-earth borotartrates are well defined compounds.[424] The atomic ratio of B:C has been shown to be 1:8.[425] $5BaO,B_2O_3,4C_4H_4O_5,10H_2O$ has a density of 2·21 and a solubility in water at 25°C of 0·7 g/l.[319] The heating curve has been determined. The structure of this borotartrate may be represented by Fig. 26; its solubility product and equilibrium constants for its formation have been determined. More recently another type of borotartrate has been synthesized, formulated as $BaC_4H_3O_5BO_2,2H_2O$.[27]

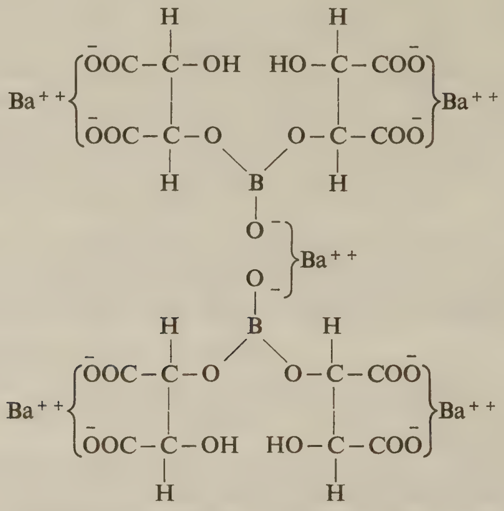

FIG. 26.—Proposed structure for barium borotartrate

Glutarate. A compound of the composition $3BaO,B_2O_3,3C_5H_6O_6,5H_2O$, having a density of 1·375 and a solubility of 3·95 g/l has been formed. Analogous strontium and cadmium compounds have also been found.[426]

Mucate. The extreme insolubility of barium boro-mucate permits the precipitation of very small concentrations of boron from solution (0·005–0·01% B) provided that SO_4^{2-} and Mg^{2+} are not present. Alkaline, alkaline-earth, and halide ions do not interfere. The procedure is to add a solution of mucic acid containing ammonia and ammonium chloride (or sodium hydroxide), to which barium chloride has been added, to the borate solution in question; the boron is then precipitated.[427]

ZINC BORATES

Anhydrous Zinc Borates

Anhydrous zinc borates have been fairly extensively investigated in conjunction with their commercial uses as luminescent materials, sealing glasses and catalysts.

Studies of the simple $ZnO–B_2O_3$ system have been somewhat contradictory in their conclusions, the solid phases reported varying according to the investigator. As will be seen below, even the 1:1 borate which seemed to have been well substantiated is now doubtful, the well-defined 4:3 borate [$Zn_4O(BO_2)_6$] having taken its place. Solid phases identified by various investigators are as follows:

(a) ZnO,B_2O_3, $2ZnO,B_2O_3$ (ref. 371);
(b) ZnO,B_2O_3, $ZnO,3B_2O_3$, $3ZnO,B_2O_3$ (ref. 428);
(c) ZnO,B_2O_3, $ZnO,2B_2O_3$, $3ZnO,B_2O_3$ (ref. 429);
(d) $4ZnO,3B_2O_3$, $ZnO,2B_2O_3$, $3ZnO,B_2O_3$ (ref. 430);
(e) α-ZnO,B_2O_3, β-ZnO,B_2O_3, α-$5ZnO,2B_2O_3$, β-$5ZnO,2B_2O_3$ (ref. 432);
(f) α-$3ZnO,B_2O_3$, $ZnO,2B_2O_3$, $4ZnO,3B_2O_3$ (ref. 600).

The orthoborate ($3ZnO,B_2O_3$) seemed to be a well-defined compound until it was suggested[432] that it might be a 5:2 borate, which was shown to have an area of existence in the $ZnO–B_2O_3–SiO_2$ system[431] (see Figs 27 and 28). Both the 1:3 and 1:2 borates appear to have incongruent melting-points, but the latter is probably better substantiated. Other anhydrous compounds described are the 2:3 and 3:2 zinc

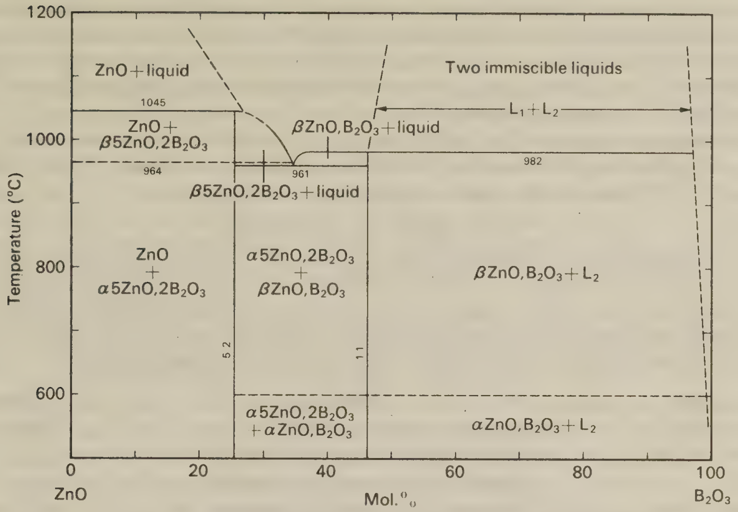

FIG. 27.—Phase diagram for the system ZnO–B_2O_3[432]

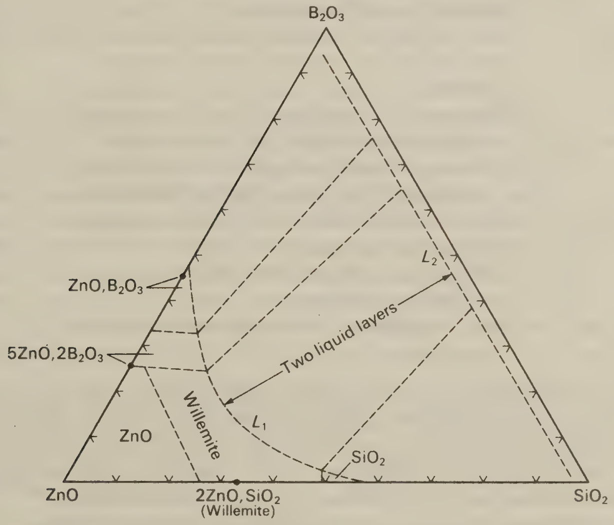

FIG. 28.—Phase diagram for the system ZnO–B_2O_3–SiO_2[431]

borates. The former has not been referred to since 1937[433] but the latter has been well investigated and was more recently proved[434] to be a mixture of the 3:1 and 1:1 borates.

As with CaO–B_2O_3, SrO–B_2O_3 and BaO–B_2O_3 systems the ZnO–B_2O_3 system also separates into two liquid layers over a range variously described as 3–48% ZnO above 990°C[428] and 0–53% ZnO.[435] The surface tensions of ZnO–B_2O_3 melts at 800–1000°C have been investigated by the author of the last reference, with the confirmation that the upper layer of the two-layer system is almost pure boric oxide; the densities are also recorded. By the addition of various oxides (of an alkali or alkaline earth, or of lead, cadmium or aluminium) in small proportions to the system the two phases were homogenized. The homogenizing action increases as the ionic radius of the added cation decreases.[2] The addition of 5% or more of silica to the system prevents devitrification.[436] The oxygen availability of the system, plotted against composition, showed a minimum which corresponds with some of the anomalous physical properties of this system. This minimum is absent after the addition of homogenizing quantities of potassium or lead oxide; this fact probably gives some clue to the reason for formation of the heterogeneous area.

The formation of an anhydrous borate by heating a precipitated hydrated borate at above 800°C has been patented.[590]

The percentage of tetra-coordinated borons in the glassy structure of the ZnO–B_2O_3 system has been determined by ^{11}B n.m.r. measurements.[381] The specific conductivity of glasses in the system conforms to the formula

$$\ln(\text{sp. cond.}) = -(A/T)+B$$

where A is approximately twice as large for zinc (cf. barium borates) as for alkali glasses and B is a constant.[374] Molar volumes and molar refractivities of ZnO–B_2O_3 glasses have been determined.[437] The coefficient of expansion and deformation temperatures were plotted against composition in the binary system ZnO–B_2O_3.[375]

Ternary systems containing zinc and boric oxides have been studied:

System	Comments	References
CaO–ZnO–B_2O_3	No ternary phases at 850°C.	396
Li_2O–ZnO–B_2O_3	Density, chemical stability and thermal expansion of glasses determined.	5
ZnO–B_2O_3–SiO_2	Existence of 1:1 and 5:2 borates.	431
	With $>5\%$ SiO_2, no devitrification.	436
	Suitable as sealing glasses.	438, 439
ZnO–PbO–B_2O_3	Very satisfactory solder glasses.	375
	Various Pb, Zn borates formed as solid phases.	440
	Structure of crystalline phases in system and effect of adding TiO_2 recorded.	441
	Decrease in volume resistivity and activation energy as crystallization proceeds.	482
	Application of differential thermal analysis to phase changes.	439
	Melts produced and tempered under different conditions.	443
ZnO–Bi_2O_3–B_2O_3	Very high refractive indices and dielectric constants.	328

Zinc borates non-activated or activated by traces of other metals (e.g. manganese) have been thoroughly investigated. Only brief mention will be given here of the phosphor role of zinc borates. Very pure zinc borate phosphors have been produced from zinc sulphide oxidized, by filtered air, to the oxide and then reacted with boric oxide. It is reported that purity is necessary for good luminescence.[444] The fluorescence intensity of manganese-activated zinc borate phosphors decreases with increasing temperature; the reasons for this have been discussed[445], and the relationship between manganese content and intensity of fluorescence has also been considered.[446] Other methods of zinc borate phosphor formation are variously described[447–50] and the properties of the phosphors discussed.[446, 451–4]

Zinc borates have an accelerating effect on reactions involving iron–copper catalyst used for the synthesis of gasoline from carbon monoxide and hydrogen.[452] They are also suitable condensing agents in aniline/formaldehyde resin formation.[551] Various other catalytic effects will be found in sections below on individual zinc borates.

A review of the war-time and commercial applications of zinc borates may be usefully referred to.[552]

ZnO,B_2O_3. This compound should be considered in conjunction with the recently identified 4:3 zinc borate. Both are called the metaborate. It is possible that the 1:1 borate referred to below is an impure form of the 4:3 borate.

The 1:1 borate was reported as a solid phase in the ZnO–B_2O_3 system. Early work indicated that there was a maximum in the cooling curve at 900°C.[371] Later workers gave melting points of 1050°C[428] and 1000°C.[429] As part of a study of the PbO–ZnO–B_2O_3 system, the ZnO–B_2O_3 system was investigated in 1956[432] (see Fig. 27) and the existence of α- and β-forms of ZnO,B_2O_3 confirmed in 1966.[440] More recently it has been suggested that the superposition of the patterns of ZnO,$2B_2O_3$ and α-3ZnO,B_2O_3 accounts for the pattern of α-ZnO,B_2O_3.[600] An area of existence in the ZnO–B_2O_3–SiO_2 system for the 1:1 borate is delineated[431] (see Fig. 28). X-Ray diffraction studies have been carried out by a number of workers[428, 429, 455], and the pattern recorded in the ASTM manual.[456] Other physical studies of the compound have been a differential thermal analysis[429], a study of the ^{11}B n.m.r. spectra of both crystalline and vitreous metaborates[457], and surface tension measurements on a 1:1 melt at its melting temperature.[458]

On cooling the molten compound from 1000°C two layers form, one of which analyses at 3ZnO,$2B_2O_3$.[459] If the 3:1 borate (orthoborate) is heated it decomposes at 900°C to give solid ZnO,B_2O_3 and a liquid containing 2% of ZnO.[428] A manganese-activated phosphor with green luminescence is produced by heating equivalent proportions of zinc and boric oxides with 5% of $MnSO_4$ at 850°C for 15 minutes. If the temperature used is 780°C some 3:1 borate is formed, regardless of the composition, which converts to the metaborate at higher temperatures.[434] A review of 1:1 (Mn) and 3:1 (Mn) zinc borate phosphors has been published.[460] Recently experiments have been carried out on the luminescent properties of some rare-earth ions partially substituted for zinc in zinc metaborate, e.g. in $Nd_{0\cdot02}Na_{0\cdot02}Zn_{0\cdot96}B_2O_4$. The glasses so formed have high optical perfection.[461]

4ZnO,$3B_2O_3$. Devitrification of melts containing 50–61% of zinc oxide in the ZnO–B_2O_3 system yields cubic crystals of the 4:3 zinc borate.[462] The temperature of devitrification is 850°C[449] and the crystals show a green fluorescence.[448] These crystals have been closely studied; chemically they contain 61% of ZnO and 39·09% of B_2O_3 (theoretical ZnO 60·93, B_2O_3 39·07%)[463], have a density of 1·2077[464] and have been analysed by X-ray[448, 463–5], infra-red[466], and n.m.r. techniques.[457] As a result of these studies, it has been shown to have an anion similar to the $(Al_3Si_3O_{12})^{3-}$ ion of sodalite (ultramarine).[462] Further to this, the boron atoms are situated at the vertices of a Fedorow's truncated octahedron, each co-ordinated to four oxygens and linked to form a three-dimensional structure.[467] Single-crystal X-ray work showed that the zinc atom is situated at the centre of a tetrahedron whose vertices are occupied by three oxygen atoms of the metaborate anions and one free oxygen.[465] On the basis of an infra-red spectral investigation this invariable four-coordination of boron is changed by fusion of the crystals.[466] The structure has been given the empirical formula $Zn_4O(BO_2)_6$. An alternative method of formation is by the thermal decomposition of ZnO,$2B_2O_3$.[600]

ZnO,$2B_2O_3$. The 1:2 zinc borate has been found in two studies of the ZnO–B_2O_3 system.[429, 430] It may also be prepared in a pure state by the action of heat on the ammine borate $[Zn(NH_3)_3H_2O]B_4O_7,6H_2O$; both ammonia and water are easily lost, leaving the zinc borate.[468] If the compound is heated above 900°C it dissociates into the 1:1 zinc borate and boric oxide.[429] X-Ray powder diffraction data are recorded by the latter authors. By annealing the borate with a slight excess of boric oxide, single crystals were obtained; these were used to study the crystal structure[588], in particular the cell dimensions of the compound, which belongs to the orthorhombic system.[589] The compound decomposes to 4ZnO,$3B_2O_3$ and boric oxide upon heating.[600] The use of this compound has been patented as a constituent which retains its fluorescent properties in a glass batch.[450] The cathodic luminescence of the manganese-activated 1:2 borate has been studied at various temperatures.[469] This borate is also described as a catalyst in the esterification of terephthalic acid with butyl alcohol.[470]

ZnO,$3B_2O_3$. In an investigation of the ZnO–B_2O_3 system by means of heating curves a solid phase was identified by X-ray diffraction studies which was chemically

$ZnO,3B_2O_3$. It had an incongruent melting-point, decomposing at 900°C to give the 1:1 borate and boric oxide containing 2% of ZnO.[428]

$2ZnO,B_2O_3$. Early work on the $ZnO–B_2O_3$ system reported two maxima in the phase diagram, both at 900°C, corresponding to the 1:1 and 2:1 borates.[371] Later the 2:1 and 3:2 borates were identified as the only compounds formed, in an investigation which involved heating boric oxide and zinc oxide together in various proportions and devitrifying at 850–900°C for 3 hours. The activating of the compound by the light from an iron arc showed a short-duration yellow afterglow.[471] Further work showed that excitation occurred with light at 2537 Å and cathode rays.[448] Glasses with a 2:1 zinc borate formulation activated with manganese gave orange luminescence.[449, 472]

$2ZnO,3B_2O_3$. Only two references are found concerning this compound, one stating that a crystalline compound activated with manganese is more phosphorescent than the glassy equivalent[473], and the other defining the effect of other ions on the crystallization of the 2:3 borate.[433] Group Ia oxides appeared to increase the crystallization, Group II oxides to slightly decrease it, and many other oxides from higher groups to markedly decrease the crystallization. Lead seemed to have no effect.

$3ZnO,B_2O_3$ and $5ZnO,2B_2O_3$. Monoclinic crystals of the orthoborate are obtained from the $ZnO–B_2O_3$ system.[429, 430, 600] It is formed by calcining a 3:1 molar ratio of zinc oxide and boric oxide at 1000°C for an hour or by heating an equimolar mixture of the oxides at 780°C; a higher temperature causes its subsequent conversion into the expected 1:1 borate.[434] Good crystals of the orthoborate have recently been isolated, the density of which was found to be 4·11. The infra-red spectrum showed that all boron atoms were in threefold co-ordination.[474] The $(BO_3)^{3-}$ triangles share a common vertex with $(ZnO_4)^{6-}$ tetrahedra. The tetrahedra form ribbons of interconnected units.[475]

A review of manganese-activated zinc orthoborates has been published[460], and a later patent describes its use in place of Zn_2SiO_4 for television picture-tube coatings.[476] It has also been patented as a catalyst in the formation of a polymer (mol) wt. ~20,000) derived from dimethyl terephthalate, dimethyl-2:5-furanedicarboxylate and ethylene glycol.[477] It is also recommended as a catalyst for a similar polymerization giving the polymer an improved affinity for dyes.[478]

It has been suggested that the 5:2 compound, which has been identified as a solid phase in the $ZnO–B_2O_3–SiO_2$ system[431], is possibly the orthoborate (see Fig. 27).[432]

$3ZnO,2B_2O_3$. Although the existence of this compound was suggested by a unique X-ray diffraction pattern[471], later workers have proved that it is almost certainly a mixture of the 3:1 and 1:1 borates. Claims for its existence have probably been based on the fact that equivalent proportions of zinc and boric oxides, when heated to 1000°C, always separate into two layers, one of which has a $ZnO:B_2O_3$ ratio of 3:2.[459]

The mixture has found use as a fluorescent composition (with violet phosphorescence)[471, 553], as a catalyst in the polymerization of dimethyl terephthalate and ethylene glycol[479], and as a condensing agent for phenolic resins.[480]

Anhydrous Borates Containing Zinc and Other Elements

Lithium. If zinc oxide is heated with excess of lithium metaborate, $Li_2O,2ZnO,B_2O_3$ crystallizes. The crystal structure has been determined, the compound has been studied by differential thermal analysis. Isostructural compounds in which zinc is replaced by cobalt or manganese have been formed.[481]

Calcium. Equilibria in the system $CaO–ZnO–B_2O_3$ were investigated at 850°C but no ternary phases were found.[598]

Lead. Compounds of the type $PbO,2ZnO,B_2O_3$, $2PbO,ZnO,B_2O_3$ and $4PbO,2ZnO,5B_2O_3$ have been isolated from the $PbO–ZnO–B_2O_3$ system by melting the constituents in differing proportions and annealing under various conditions. X-Ray studies were made of these compounds.[440] As the system crystallized, the volume resistivity and activation energy of electrical conduction decreased. In the system $PbF_2–ZnO–B_2O_3$ these factors increased during crystallization, but at higher temperatures the oxyfluoride crystals transformed into $PbO,2ZnO,B_2O_3$ and the variables decreased.[482]

Phosphate. The preparation of zinc borophosphate glasses has been recorded.[483]

Sulphate. The compound $Zn[B(SO_4)_2]_2$ is formed by reaction of zinc sulphate and boric acid with sulphur trioxide. It is colourless, hygroscopic and ionic in structure with a large polymeric anion.[11]

Chloride. A compound of the same structure as boracite is formed in the usual manner (*v.* Boracite) by heating zinc chloride, zinc oxide, and boric oxide at a temperature above 300°C in a closed container, together with a gaseous-phase carrier (H_2O, HX, O_2, or X_2, where $X =$ halogen).[45] The structure of this compound is $Zn_3[B_7O_{13}]Cl$ and it is classified in the same group as the 4:3 borate, $Zn_4[B_6O_{12}]O$, a three-dimensional lattice borate[556]: (see β-boracite in magnesium borate section).

Hydrated Zinc Borates

The formation of well-characterized hydrated zinc borates at normal temperatures is resisted, only two borates ($2ZnO,3B_2O_3,7H_2O$ and $2ZnO,3B_2O_3,7\frac{1}{2}H_2O$) being formed in a crystalline form at 20°C[484] and $2ZnO,3B_2O_3,3\frac{1}{2}H_2O$ above 70°C.[21] A number of hydrated zinc borates are formed under hydrothermal conditions. More complex borates containing ammonium or potassium ions are formed with comparative ease. The presence of excess ammonia and boric acid during precipitation is recommended when zinc borate from a zinc sulphate solution is used as an intermediate in the production of anhydrous zinc borate by heating the precipitate above 800°C.[590] The precipitation of amorphous zinc borates in relation to the pH of the reaction mixture has been studied at room temperatures[485]; earlier work indicated that borate precipitation occurred at the same pH as formation of the hydroxides.[30] Some evidence has been found for pentaborate formation in solution.[486]

Zinc borates have been used as insecticides or anti-cryptogamics[487–8], and as brighteners to lead/zinc chromate pigments.[489] They have also been precipitated from Chile saltpetre solutions to remove traces of borate found therein.[490] The properties and uses of zinc borates have been reviewed.[491]

Sols may be formed essentially consisting of zinc borate; the change in viscosity with time in such sols has been studied in some detail.[492]

ZnO,B_2O_3,H_2O. When 0·15N borax solution is added to an equal volume of 0·1N zinc nitrate, an amorphous precipitate is formed which crystallizes after 24 hours. Its solubility product is $5{\cdot}56 \times 10^{-11}$ and its solubility in 0·5N boric acid is 270 times the solubility in water. This observation, together with an instability constant of $1{\cdot}61 \times 10^{-12}$, suggests complex formation represented by the following equation[493]:

$$Zn(BO_2)_2 + 2H_3BO_3 \rightleftharpoons H_2[Zn(BO_2)_4] + 2H_2O.$$

$2ZnO,3B_2O_3,3{\cdot}5H_2O$. The production of this hydrate of the 2:3 zinc borates has been patented.[362, 423] It is formed by a method similar to that employed for the $7\frac{1}{2}$ hydrate (see below and ref. 21), except that higher temperatures are used (>70°C). Alternatively it is produced by adding slowly a mixture of powdered zinc oxide and boric acid to a boric acid solution at a temperature above 70°C. A similar product has been obtained by reaction of zinc hydroxide with boric acid or metaboric acid at 100–260°C.[362] The compound has a distinct X-ray powder pattern, the crystals being irregular and diamond-shaped[423] with a density of 2·69.[205]

The water of hydration is completely retained up to 260°C. The compound hydrolyses very slowly in cold water, the degree of hydrolysis increasing slightly with rise in temperature to yield eventually a solution containing 1% of B_2O_3.[205]

It has been quoted specifically in a patent[541] as an effective fire retardant for chlorinated polyesters.

$2ZnO,3B_2O_3,7H_2O$ ($7\frac{1}{2}H_2O$). A recent investigation of the $ZnO–B_2O_3–H_2O$ system at 20°C[484] suggests that the only solid phases present in the system are $2ZnO,3B_2O_3,7H_2O$ and $2ZnO,3B_2O_3,7\frac{1}{2}H_2O$. These two compounds have the same X-ray powder diagram and infra-red spectrum but appear to have distinct formulae. A heptahydrate is supported by the formula $Zn[B_3O_3(OH)_5]H_2O$ assigned to the orthorhombic crystal, which consists of isolated $B_3O_3(OH)_5^{2-}$ anions.[599]

A patent exists[495] for the production of the heptahydrate by reaction of zinc sulphate with borax and later addition of zinc oxide or a mixture of sodium hydroxide and zinc sulphate. The reaction is carried out at room temperature and with a borax concentration above the solubility of borax at ambient temperatures. The overall ratio of $ZnO:B_2O_3$ is somewhat greater than 2:3.

By heating zinc sulphate with borax and boric acid in the ratio borax:$ZnSO_4$: boric acid = 1:1:10, an initial flaky-white precipitate forms, which alters in time to give needle-shaped crystals of $2ZnO,3B_2O_3,7\frac{1}{2}H_2O$. The factors which increase the rate of crystallization are heat, agitation and excess boric acid.[21] The latter factor controls the pH during the crystallization and is most important.[495] The same product is obtained by reacting boric acid with zinc sulphate and ammonium hydroxide solution and drying the precipitate at 100–110°C.[597] The density of the product is 2·44 and its dehydrates on heating between 120° and 170°C, when 6 molecules of water are lost; the remainder is lost slowly on heating to 400°C to give the anhydrous product (density 2·88). Hydrolysis is slow at room temperature.

The heptahydrate has been suggested for flameproofing of fabrics.[494]

$3ZnO,5B_2O_3,14H_2O$. The reaction of zinc acetate in the following way produces a compound of the above composition[496]:

$$3Zn(OAc)_2 + nH_3BO_3 + 2H_2O \rightleftharpoons 3ZnO,5B_2O_3,14H_2O + 6AcOH + (n-10)H_3BO_3.$$

The compound is slightly soluble in water, with hydrolysis, but does not hydrolyse in dilute boric acid solutions. It dissolves to the extent of 0·83 g/l at 25°C in 3% boric acid and 1·68 g/l in 5% boric acid. It loses $1H_2O$ at 60°C, $11H_2O$ between 70° and 120°C, and $2H_2O$ slowly up to 300°C.

Other Hydrated Binary Borates

The compounds $ZnO,5B_2O_3,4{\cdot}5H_2O$; $2ZnO,3B_2O_3,3H_2O$; $6ZnO,5B_2O_3,3H_2O$; are formed hydrothermally.[484]

Hydrated Zinc Borate Containing Other Elements

Potassium. By mixing zinc sulphate with potassium tetraborate ($K_2O,2B_2O_3,4H_2O$) in the molar ratio 1:3·5 (thus maintaining a pH of 8·5 for the crystallization) the amorphous compound $K_2O,2ZnO,5B_2O_3,10H_2O$ is formed initially; on standing for 3–4 days this crystallizes into the 16 hydrate. The compound has a density of 2·31 and is very slow to hydrolyse. Differential thermal analysis has been carried out on this hydrate.[499]

Tartrate. A crystalline zinc borotartrate is precipitated if a solution of boric acid (0·1 mole), tartaric acid (0·16–0·32 mole) and potassium hydroxide (0·133 mole) in 200 ml of water is treated with 0·01 mole of zinc sulphate. The pH is maintained at 7·8 (or greater than 11) by the addition of potassium acetate and acetic acid (or potassium acetate and hydroxide) buffers. The compound corresponds to the formula $3ZnO,B_2O_3,2C_4H_4O_5,3H_2O$. It has a density of 2·04 and a solubility of 3·7 g/l at 18°C. Water of crystallization is lost at 230–284°C and the organic radical ignites between 413° and 625°C.[500]

Ammonium. As well as $4ZnO,2B_2O_3,4NH_3,6H_2O$ (Mellor, V, p. 10) the compound $(NH_4)_2O,ZnO,6B_2O_3,10H_2O$ may be crystallized in 1–2 days from a mixture of ammonium tetraborate, boric acid and zinc sulphate in aqueous solution at 40°C.[497] Its crystals are triclinic, and its optical properties are recorded. An isomorphous potassium-cadmium compound is also formed. Both compounds lose their water of crystallization between 70° and 300°C and slowly hydrolyse in water (but not in dilute boric acid). The density of the ammonium zinc borate is 1·90.[497]

Another ammonium zinc borate, probably isomorphous with $K_2O,2ZnO,5B_2O_3,10H_2O$ and of analogous formula ($(NH_4)_2O,2ZnO,5B_2O_3,10H_2O$) has been prepared; its density is 2·29.[498]

A zinc ammine borate, $[Zn(NH_3)_3H_2O]B_4O_7,6H_2O$, has been prepared, and in a similar manner the cadmium analogue. Its general properties and thermal stability are reported. It is suggested as a good starting material for the formation of the anhydrous 1:2 zinc borate by heating it to drive off both ammonia and water.[468]

Another borate containing the ammonium radical and zinc has been formed, but in this case the structure is further complicated by the addition of mucate radicals. It is prepared by adding a boric acid and mucic acid mixture (in a 1:1 or 1:2 ratio) to a zinc nitrate solution containing ammonia. The compound $(NH_4)_2O,3ZnO,B_2O_3,2C_6H_8O_7,5H_2O$ crystallizes from the reaction mixture. It has a solubility of 5·17 g/l. Its dehydration and de-ammination have been studied.[501]

CADMIUM BORATES

Anhydrous Cadmium Borates

Virtually all the interest in anhydrous cadmium borates has arisen from their fluorescent properties. As with most borate systems of Group IIa and IIb elements, two liquid phases are found at temperatures above the liquidus, which can be homogenized by the addition of other oxides or further cadmium ions.[2] The solid phases obtained from the system are the 3:1, 2:1, and 2:3 borates. These have been identified in the system using techniques of high-temperature microscopy combined with X-ray data and D.T.A.[502] The authors of this work state that they could not obtain the 3:2 compound which other workers had isolated in previous investigations (see Fig. 29).[503, 575] Earlier investigations also suggested the existence

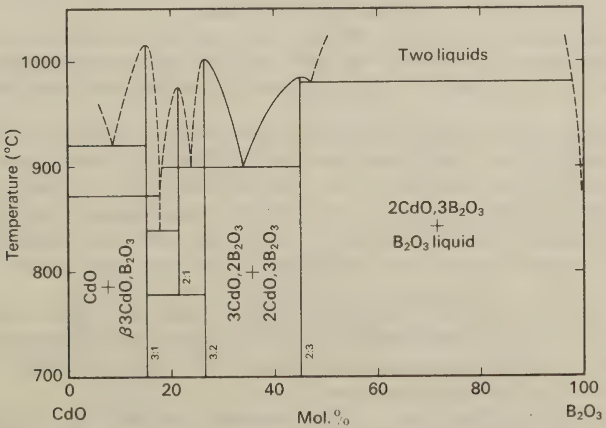

FIG. 29.—Phase diagram of system $CdO–B_2O_3$[575]

of the 1:1 borate in the system[504–5] but it seems not to be a stable phase. Quite recently the 1:2 borate has been characterized.[506] Physical properties of the anhydrous borates have been generally discussed.[507]

The polarographic behaviour of cadmium oxide dissolved in sodium tetraborate at 820°C agreed with the equation $i_d = kN$, as does the behaviour of many other oxides in molten borax; N is the molar fraction of CdO.[433] The refractive indices and specific gravities of simple $CdO–B_2O_3$ glasses have been determined[437] and the X-ray scattering curves of the glasses shown to be very similar to strontium and barium borate and barium borosilicate glasses.[332]

The formation of cadmium borate phosphors together with other phosphorescent borates, has been described.[18] Heat treatment of mixtures of cadmium carbonate and ammonium biborate ($(NH_4)_2O,2B_2O_3,4H_2O$) produces cadmium borate phosphors.[508] The fluorescence of cadmium borates related to various activating wavelengths, has been investigated[509–11], and applied to the formation of fluorescent screens.[511–12] The effect of temperature on the intensity and frequency of emission spectra has been well studied.[445, 513–16] The addition of fractional percentages of manganese activates the intensity of the phosphorescence. Some of these activated phosphors glow red and have been used to correct the colour of mercury-discharge fluorescent lights.[517] The addition of silica to activated borates has been studied by its effect on after-glow.[518] The quantum efficiency of manganese activated cadmium borates has been determined.[519] An appreciable amount of work has also been carried out on the fluorescent properties of mixtures of cadmium borates with zinc borate[452], magnesium tungstate and zinc silicate[520, 521], calcium halophosphoarsenate, or arsenate[522] and calcium tungstate, etc.[478]

The fusibility diagram of the $Li_2O–CdO–B_2O_3$ system has been described and the principal properties of the glasses determined.[5] The reactions in the system $CdO–Ga_2O_3–B_2O_3$ have been studied by using D.T.A., microstructural density, microhardness and conductivity measurements.[591]

CdO,B_2O_3. Fragments of a crystalline metaborate have been identified.[504] An investigation of the $CdO–B_2O_3$ system resulted in the reported formation of the 1:1 compound as a crystalline phase, m.p. 875 ± 5°C[505, 523], but it appears not to be an easily formed solid phase in the system, as later workers were unable to obtain it.[502]

Solid-phase reactions have been studied between anhydrous zinc and cadmium metaborates by heating in close contact discs of each material and studying the type of fluorescence in each surface after the treatment, thus showing the direction of diffusion.[453] Studies of the reaction of cadmium metaborate with magnesium, calcium and barium metaborates at high temperatures resulted in the formation of various compounds[7]; the composition and melting points of these are given in sections above on the various alkaline-earth borates.

Manganese-activated metaborate shows only a green cathodoluminescence.[453] Photoconduction currents are reported both for the manganese-activated and unactivated cadmium 1:1 borate.[525] The quantum output has been studied.[526]

$CdO,2B_2O_3$. Quite recent work has resulted in the formation of this compound and X-ray diffraction data have been recorded.[506] Further crystal studies enabled a three-dimensional Fourier analysis to be made showing the structure to consist of two interlocking networks built up from a single type of borate unit composed of four borate polyhedra. Half of the boron atoms are tetra-co-ordinated and each cadmium ion is surrounded by four oxygens in a distorted tetrahedron.[528]

$2CdO,B_2O_3$. This compound, which has been formed as a solid phase in three investigations of the $CdO–B_2O_3$ system[502, 503, 505], has a melting point of 980°C.[523] X-Ray powder diffraction data have been collected.[506] Crystals of $2CdO,B_2O_3$ form easily from the $CdO–La_2O_3–B_2O_3$ system.[529]

Manganese-activated phosphors of this composition have an orange luminescence[505, 530] and a maximum emission at 6150 Å.[531] It has been shown that the orange emission consists of three components.[532] The intensity of emission decreases steadily below −100°C but remains steady above this temperature, when using an activated quartz heavy-vapour lamp.[533] It shows thermoluminescence after excitation with ultra-violet irradiation of wavelengths between 2480 and 3120 Å.[592]

The effect of silica on decay characteristics of this phosphor[534] and the afterglow effect by the addition of bismuth have been investigated.[535] Studies of intrinsic efficiency[536–7], absorption coefficient[537] and quantum yield[536–7] of cadmium metaborate phosphors have been carried out. A general discussion of dissipation processes may be referred to.[539] More work seems to have been performed on this cadmium borate phosphor than on the others described here; it has in fact been described as a 'common phosphor'.[533]

$2CdO,3B_2O_3$. In all the recent studies of the $CdO–B_2O_3$ system, this compound is found[502–5, 591] and may be regarded as the easiest to obtain. Very little work has been done on its use as a phosphor. It does, however, show a green cathodoluminescence when activated with manganese.[505] Its melting point is 980°C.[523]

$3CdO,B_2O_3$. This compound is also a well substantiated solid phase of the $CdO–B_2O_3$ system[502–3, 505] and like the 2:3 phosphor shows green cathodoluminescence.[505] Its use as a luminous pigment has been suggested.[540] Some attempt to determine its structure has been made by study of the infra-red spectrum of the crystalline compound.[73] It has a melting point of 1020°C.[523]

$3CdO,2B_2O_3$. One investigator obtained this compound as a solid phase of the $CdO–B_2O_3$ system[503] but a subsequent worker could not prepare it.[502] Like the 2:1 borate it fluoresces orange when activated with cathode rays.[503]

The melting point is 1005°C.[523]

Anhydrous Cadmium Borates Containing Other Elements

Lithium. The complete phase diagram has been prepared for the system $Li_2O,B_2O_3–2CdO,3B_2O_3$.[596]

Zinc. Two ternary compounds $2CdO,ZnO,B_2O_3$ and $CdO,2ZnO,2B_2O_3$ have been isolated from the $ZnO–CdO–B_2O_3$ system[268] (see Fig. 30). Their optical, thermal, fluorescent and X-ray diffraction properties were determined.

Tin. A compound with a dolomite structure[10] of the formula $CdSn(BO_3)_2$ has been synthesized.[344]

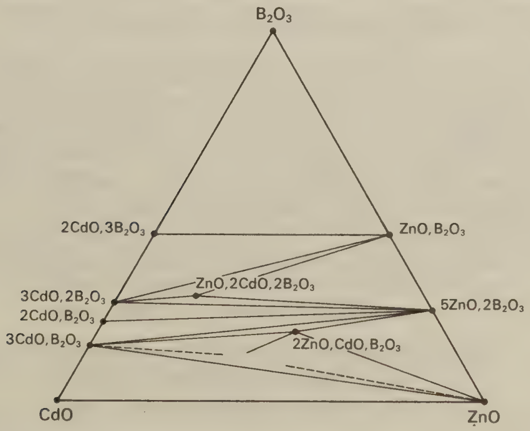

FIG. 30.—Phase diagram for the system $CdO–ZnO–B_2O_3$ (Compatibility triangles)[268]

Zirconium. CdO,ZrO_2,B_2O_3 is one of the group MO,ZrO_2,B_2O_3 (where M = Ca, Sr, Ba, Cd) which has been formed by cooling mixed oxide melts.[538]

Vanadium. Boron and vanadium occur together in a series of salts with bivalent metals in which the M:V ratio can be 1:1 or 1:2. When M is Cd, then $2CdO,V_2O_5,3B_2O_3$ is formed only when cadmium oxide, carbonate or hydroxide is fused at 1000°C with vanadium pentoxide and boric oxide for $3\frac{1}{2}$ hours, with the latter 10% in excess over the stoichiometric quantity. If the $CdO:V_2O_5$ ratio is 1·25, then CdO,V_2O_5,B_2O_3 is formed after several hours heating. Both of these compounds hydrolyse readily.[221]

Sulphur. The colourless hygroscopic compound $Cd[B(SO_4)_2]_2$ is formed by the reaction of cadmium sulphate, boric acid and sulphur trioxide (in the molecular proportions 1:2:6). It is probably ionic with a high-polymer anion.[11]

Halogens. Cadmium boracites are formed (in an analogous fashion to similar compounds of magnesium and zinc) by reaction of a halide of cadmium with cadmium oxide and boric oxide at 300°C, in an autoclave. The compound forms on the colder surface of the autoclave and is produced by a vapour-phase reaction needing a hydrogen halide, oxygen or water vapour carrier.[45]

Hydrated Cadmium Borates

Apart from $CdO,2B_2O_3,2H_2O$, synthesized by Ditte[542] in 1883, and a rather ill-defined compound corresponding to $3CdO,2B_2O_3,3H_2O$ (Mellor, V, 101), the only two simple hydrated cadmium borates produced and characterized are CdO,B_2O_3,H_2O and $CdO,2B_2O_3,5H_2O$. Further than this, evidence exists for the formation of a solution containing cadmium ions and pentaborate ions.[486] More recently a 2:3:7 compound has been synthesized.

Complex cadmium borates appear to be synthesized with less difficulty than those, for example, of zinc.

CdO,B_2O_3,H_2O. Cadmium 1:1 borate monohydrate is formed by adding 0·15N borax solution to an equal volume of a hot 0·1N solution of cadmium nitrate; the amorphous precipitate crystallizes in 24 hours.[22] The product has a solubility product of $2{\cdot}31 \times 10^{-9}$ in 3% boric acid solution. As the boric acid concentration increases, so the compound increasingly dissolves, until in 0·5M boric acid it is nine times as soluble as in water. It has been suggested that the complex formation in solution could be represented by:

$$Cd(BO_2)_2 + 2H_3BO_3 \rightleftharpoons H_2[Cd(BO_2)_4] \quad \text{(cf. zinc metaborate).}$$

The compound, on this basis, has an instability constant of $2{\cdot}3 \times 10^{-11}$.[493]

$CdO,2B_2O_3,5H_2O$. This hydrate is the best-characterized borate of cadmium and is prepared by displacing acetic acid from cadmium acetate by the addition of boric acid. A hot saturated boric acid solution is added to an equal volume of an aqueous cadmium acetate (in a 4:1 molar ratio) with constant stirring and heating until the smell of acetic acid disappears (some days). Needles of the 1:2:5 borate are precipitated, and can be recrystallized from a large volume of 0·1N acetic acid buffered with cadmium acetate.[21, 543] One molecule of water is lost at 100°C, and a further 3 at 100–150°C, and the last molecule is retained up to 300°C at which it is lost slowly. The crystals hydrolyse on long standing in water. As with the 1:1:1 borate the solubility is increased by the presence of boric acid,

e.g., in 2% H_3BO_3 the solubility is 0·68 g/l;
3% H_3BO_3 the solubility is 1·02 g/l;
5% H_3BO_3 the solubility is 1·59 g/l.

The mobility of the anion in a 3% boric acid solution is 16·2 mho/cm^2.[544]

The structure has been studied and found to belong to the class of double-ring borates with independent polyions[63], represented as $Cd[B_4O_5(OH)_4],3H_2O$[21]; this does not obviously agree with the dehydration data.

$2CdO,3B_2O_3,7H_2O$. Only brief reference is made to the formation of this compound.[545]

Hydrated Cadmium Borates Containing Other Elements

Ammonium. The complex compound $[Cd(NH_3)_2(H_2O)_2]B_4O_7,5H_2O$ has been synthesized in a similar manner to the almost analogous zinc ammonium borate $[Zn(NH_3)_3H_2O]B_4O_7,6H_2O$. The general properties are discussed. It is recommended as a suitable starting point for the production of pure $CdO,2B_2O_3$.[468]

A more complex compound containing the ammonium radical and the trihydroxyglutarate radical has been prepared and has the formula $2CdO,(NH_4)_2O,B_2O_3,$-$2C_5H_6O_6,9H_2O$.[546] The density is 1·904. It is hydrolysed in water.

Potassium. If solutions of potassium tetraborate ($K_2B_4O_7,xH_2O$), boric acid and cadmium sulphate are mixed at 50°C there is a rapid precipitation of $K_2O,CdO,$-$6B_2O_3,10H_2O$, isomorphous with $(NH_4)_2O,ZnO,6B_2O_3,10H_2O$ (*q.v.*).[497] It crystallizes in triclinic form and contains one molecule per unit cell. It starts to lose water at 70°C, and dehydration is complete at 300°C. It hydrolyses slowly in water but is stable in dilute boric acid solutions.

Trihydroxy Glutarate. In addition to the complex ammonium cadmium borate containing the trihydroxyglutarate radical, the simpler compound $3CdO,3B_2O_3,$-$2C_5H_6O_6,9H_2O$ has also been prepared. It has a density of 2·47 and is soluble in water at 25°C to the extent of 7·05 g/l.[546]

MERCURY BORATES

Simple mercury borates are not formed under normal conditions of reaction, and it is only very recently that a mercury borate has been synthesized. It was formed from its oxides by reaction at 700–940°C under a pressure of 24–40 kilobars.[547] The only borate so far prepared is the 4:3 borate $4HgO,3B_2O_3$, which is isostructural with the analogous 4:3 zinc borate or 'metaborate' (*q.v.*). The boron atoms in the structure are tetra-co-ordinated, as established by study of the infra-red spectra. It decomposes at 360°C in a stream of hydrogen, forming both α- and β-boric oxides. It is more stable than mercuric oxide but decomposes at 565°C under vacuum.

Apart from this borate there are a few compounds which contain both mercury and boron together with other elements or groups. There is reference to phenyl mercuric borate being toxic to *Candida albicans*.[548] Phenyl mercuric acetate is used extensively as an intermediate in the familiar mercuration substitutions in organic syntheses; the borate is probably formed by substitution for the acetate radical.

A highly explosive compound 'Hg_2N borate'[549] is said to be formed by double decomposition between the nitrate $Hg_2N.NO_3$) and ammonium, sodium or potassium borate. Radicals other than borate also form these explosive compounds. A compound $Hg[B(SO_4)_2]_2$ is formed by the reaction of mercuric sulphate with boric acid and sulphur trioxide.[11] Analogous compounds in Group IIa and b are formed (*q.v.*). By adding mercuric oxide (2 moles) to a mixture of 2 moles of alkyl chloride, 10 moles of water and 2 moles of acetic acid, allowing reaction to proceed for 30 minutes the compound $ClCH–CH_2HgH_2(BO_3)_2O$ is obtained.[550]

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BORATES OF GROUP III

ALUMINIUM BORATES

Anhydrous Aluminium Borates

The importance of both aluminium and boric oxides in glass formation has led to the fairly extensive study of a variety of complex systems containing these oxides. The simple system Al_2O_3–B_2O_3 has also been investigated, but until 1960 no solid phases had been positively identified. Two borates were then fairly well confirmed as existing throughout a large range of the Al_2O_3–B_2O_3 system[1]: $9Al_2O_3,2B_2O_3$ and $2Al_2O_3,B_2O_3$. Glass formation areas in the Al_2O_3–B_2O_3 system have also been determined[2] and the structure of aluminoborate melts at 1600°C investigated.[3] A tentative phase diagram of the Al_2O_3–B_2O_3 system has been drawn up between 600° and 1650°C[4], confirming the two solid phases mentioned above (see Fig. 31). The system was studied in conjunction with the ternary system Li_2O–Al_2O_3–B_2O_3[5] (see Fig. 32) and the quarternary system Li_2O–B_2O_3–Al_2O_3–SiO_2.[6]

The thermodynamics of the Al–B–O system have been investigated with special reference to vaporization studies of various compositions in the system and its application to rocket propulsion.[7–11]

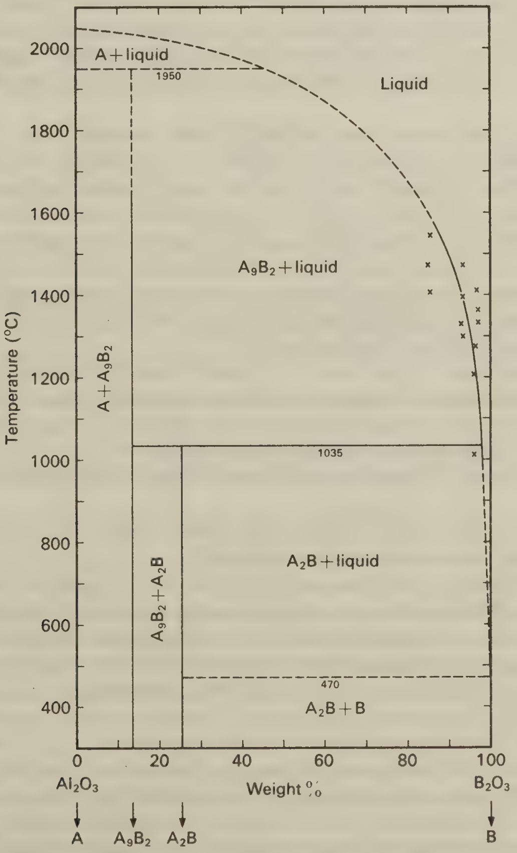


FIG. 31.—Phase diagram of the system Al_2O_3–B_2O_3[4]. $A = Al_2O_3$, $B = B_2O_3$

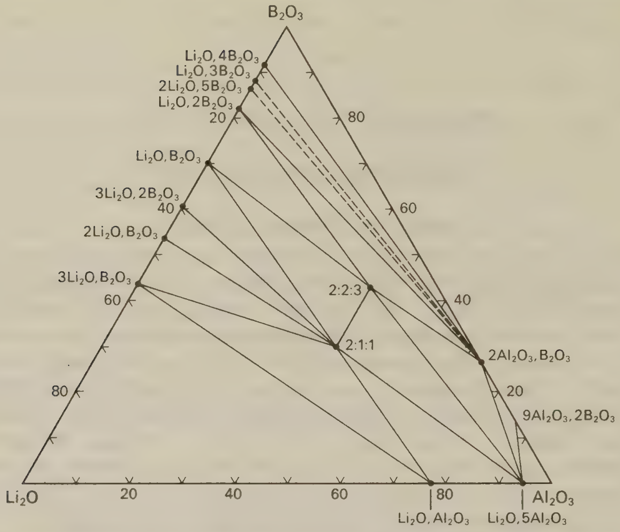


FIG. 32.—Phase diagram of the system Li_2O–Al_2O_3–B_2O_3 (Compatibility triangles)[5]

Aluminium borate whiskers, of three different types, have been grown by two methods, one via the vapour phase at 1175–1225°C (which gave whiskers between 0·2 mm and 27 mm long) and the other via the liquid phase (giving slightly shorter fibres, 0·2 mm–20 mm). The melting points of these fibres ranged from 1675° to 1795°C.[12] Molten boric oxide and borax were used as suitable solvents and sources of B_2O_3.

The 9:2 aluminium borate was probably first isolated from the system Li_2O–Al_2O_3–B_2O_3, which was particularly studied to determine the regions of easily fusible glasses. Many physical properties of these glasses were studied to aid the formulation of certain theories of the two networks which occur in the system.[13] Further study of the Li_2O–Al_2O_3–B_2O_3 system showed the presence of the 2:1 aluminium borate as well as the 9:2.[5] The solid phases of the CaO–Al_2O_3–B_2O_3 system have been determined.[14] A glass formation study was made[15], and the co-ordination of the boron atoms therein deduced to be four-fold by n.m.r. studies.[16] The BaO–Al_2O_3–B_2O_3 system has also been studied.[114]

Boric oxide additions to the field of primary mullite ($3Al_2O_3,SiO_2$) only lowers the liquidus temperature of phase equilibria slightly.[27] Mixed crystals of mullite and the 9:2 aluminium borate are formed in the Al_2O_3–B_2O_3–SiO_2 system.[26] A later study of the latter system has also been made.[17]

No glass formation is found in either the Al_2O_3–TiO_2–B_2O_3 or Al_2O_3–ZrO_2–B_2O_3 systems.[2]

The Li_2O–Al_2O_3–B_2O_3–SiO_2 system has been studied with particular reference to the areas which make good sealing glasses.[113]

Quenching methods of studying a glass have been used on the system Y_2O_3–Al_2O_3–PbO–B_2O_3–PbF_2 to distinguish the stable crystallization areas.[18]

Many other systems containing aluminium and boric oxides have been studied for glass formation properties and are discussed elsewhere (Section E1). Doping of $AlBO_3$ with traces of chromium give pink crystals, similarly to the formation of ruby from corundum.[151]

Al_2O_3,B_2O_3. This has been accepted as the formula of the mineral *jeremejevite* but it has recently been suggested that there is better agreement with the formula $Al_6B_6O_{15}(OH)_3$.[19] Synthesis of the 1:1 borate had failed[1] until very lately, when an anhydrous borate identical with jeremejevite has been formed[20] and the formula Al_2O_3,B_2O_3 attributed to it. A borate of this ratio was obtained by hydrothermal synthesis at high pressure.[140] Thermal decomposition of the trihydrate has been studied.[142]

$2Al_2O_3,B_2O_3$. The 2:1 aluminium borate is found over a range of compositions (20–80 wt.-% B_2O_3) in the Al_2O_3–B_2O_3 system when heated at 800–900°C for 18 hours.[1] It is more specifically prepared by heating 3 parts of alumina with 7 parts of boric acid by weight for 70 hours at 1000°C[21] or by the calcination of mixtures of boric acid and aluminium nitrate or sulphate at 1000–1100°C.[138–9] The melting point is incongruent and is quoted as 1030 ± 7°C by workers studying the Al_2O_3–B_2O_3 system in a preliminary investigation of the Li_2O–Al_2O_3–B_2O_3 system.[5] Earlier workers quoted 1050°C as the melting point and recorded, among other physical data, a density of 2·93.[21] A study of the system Al_2O_3–B_2O_3–H_2O between 100° and 300°C showed $2Al_2O_3,B_2O_3$ as the only solid phase borate[132] (see Fig. 33). This was confirmed as the ultimate product in hydrothermal synthesis.[141]

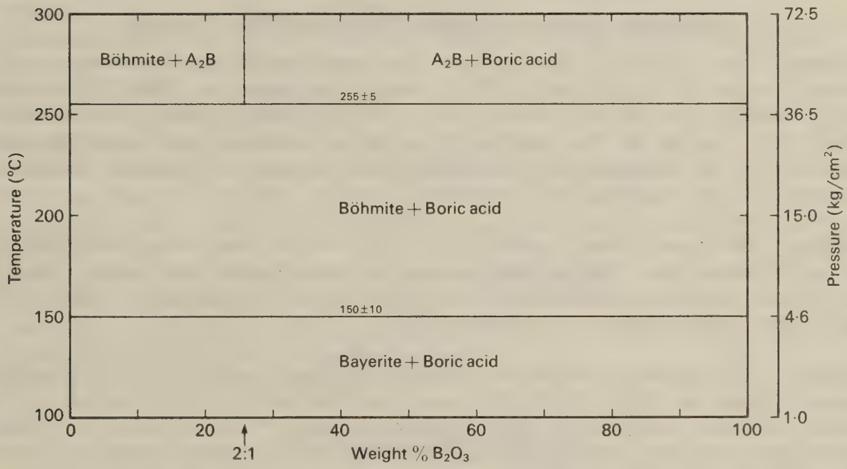


FIG. 33.—Phase relationships in the system Al_2O_3–B_2O_3–H_2O[132]

This borate has been studied as a source of an inorganic fibre.[22] It decomposes to $9Al_2O_3,2B_2O_3$ at 1100–1200°C.[138–9] Other fibres of more indeterminate $Al_2O_3:B_2O_3$ ratios have been produced, one with a ratio 2·5:1 being the nearest to 2:1.[12]

$3Al_2O_3,2B_2O_3$. The compound was formed under hydrothermal conditions.[141]

$3Al_2O_3,4B_2O_3$. This compound has recently been synthesized by hydrothermal methods; its structural features and thermal stability were studied.[112]

$5Al_2O_3,3B_2O_3$. This is formed in the Al_2O_3,B_2O_3 system on heating at 800–1000°C.[135]

$9Al_2O_3,2B_2O_3$. Like the 2:1 borate the 9:2 aluminium borate is identifiable over a wide range of the Al_2O_3–B_2O_3 system (20–90 wt.-% B_2O_3) at 1100°C.[1] One part of boric oxide dissolved in 4 parts of molten alumina in an electric furnace produces orthorhombic crystals of $9Al_2O_3,2B_2O_3$ by heating the mixture at 1100°C for 70 hours.[21] The compound is also formed at lower temperatures by heating aluminium with anhydrous borax at 960°C for 48 hours, or by heating $2Al_2O_3,B_2O_3$ with aluminimum in anhydrous borax at 940°C.[23] In an investigation of the Li_2O–Al_2O_3–B_2O_3 system, the 9:2 borate was the only detectable solid phase other than lithium borates[13], but see above.[5] Two forms of the 9:2 borate appear to exist with incongruent melting-points of 1440° and 1950°C.[24] Physical properties and X-ray diffraction details are available for both modifications.[21, 25]

Its other properties appear to be somewhat analogous to those of mullite ($3Al_2O_3,SiO_2$). It is insoluble in water and quite stable[25] and forms a solid solution[26] with mullite at 1200°C, the mixed crystals from which are more resistant to hydrogen fluoride than mullite alone.[27]

Aluminium borate whiskers have been produced with a formula slightly different from $9Al_2O_3,2B_2O_3$, namely $4{\cdot}8Al_2O_3,B_2O_3$.[12]

Other Binary Aluminium Borates

Apart from indeterminate aluminium borate whiskers analysing at $2{\cdot}5Al_2O_3$,-B_2O_3,$3{\cdot}8Al_2O_3,B_2O_3$ and $4{\cdot}8Al_2O_3,B_2O_3$[13] other fibres have been formed. $(Al_2O_3)_{3\pm0{\cdot}4},B_2O_3$ is formed by heating a 4:1 mixture (by weight) of boric oxide and aluminium hydroxide at 1400°C, cooling it in a controlled manner and digesting with 2% sodium hydroxide solution. If the product is heated at 1750°C for 5 minutes $(Al_2O_3)_{9\pm0{\cdot}4},B_2O_3$ is formed. The fibres of the latter composition thus produced were 0·7 mm long and had a length:breadth ratio of 10:1.[28]

Anhydrous Aluminium Borates Containing Other Elements

Lithium. The Li_2O–Al_2O_3–B_2O_3 system has been studied, and two ternary solid phases discovered: $2Li_2O,2Al_2O_3,3B_2O_3$ which decomposes at 790±20°C to give the 1:5 lithium borate and a liquid, and $2Li_2O,Al_2O_3,B_2O_3$ which melts at about 870°C. The nature of this reaction is unknown.[5] $3Li_2O,Al_2O_32B_2O_3$ has been described.[136] Its structure is monoclinic and consists of infinite chains of $[Al_2(BO_3)_4]^{6-}$ and bands of Li^{4+} tetrahedra.

Sodium. The pseudobinary system Na_2O,B_2O_3–Al_2O_3 has been investigated by X-ray diffraction and infra-red spectroscopy. A solid phase of composition Na_2O,-Al_2O_3,B_2O_3 is present at 40–60 mol.-% Al_2O_3. It has a melting point of 1010±10°C and a pycnometric density of 2·62 g/cm^3.[123]

Calcium. Two ternary compounds have been isolated from the CaO–Al_2O_3-B_2O_3 system. These are $2CaO,Al_2O_3,B_2O_3$ and CaO,Al_2O_3,B_2O_3.[14] Aluminium in the system has been confirmed as being hexa-co-ordinated.[29] The structure of $2CaO$,-Al_2O_3,B_2O_3 has been investigated and may be more logically written as CaAl-(O/BO_3).[30]

Magnesium. $Al_2O_3.2MgO.B_2O_3$ was prepared by hydrothermal synthesis.[144]

Lead. Supercritical fluctuations in the B_2O_3–PbO–Al_2O_3 system have been studied.[143]

Lanthanides (Rare Earths). Borates of the general formula $LnX_3(BO_3)_4$, where Ln = yttrium or a lanthanide element and X is aluminium or chromium, have been synthesized during the past few years. Many of the compounds containing lanthanide and aluminium are fluorescent when activated with ultra-violet light, and most have piezoelectric properties.

Crystallization of these borates is usually accomplished by use of molybdenum trioxide and potassium sulphate or lead borate, $Pb_3(BO_3)_4$ fluxes, although a PbF_2–B_2O_3 mixture has been used for $YAl_3(BO_3)_4$.[146] Compounds have been produced where Ln = Y, Gd, Er, Sm, Nd, Dy, Tb, Ho, Eu[31–2], and Yb, Ho, Er[33], the former using the MoO_3/K_2SO_4 flux and the latter using a $MoO_3/Pb_3(BO_3)_4$ flux. Potassium molybdate and PbO–B_2O_3 were later used for Ln = Pr and Nd.[148]

The crystals have a trigonal-rhombohedral lattice[31] and are isostructural with the carbonate mineral *huntite*.[32] Lattice constants, densities and unit-cell volumes have been calculated, showing that the familiar lanthanide contraction occurs with the borates as the atomic number of the rare-earth ion increases.[33] As an indication of the properties of these borates the compound $YAl_3(BO_3)_4$ has a hardness of 7·5 Mohs and density 3·7.[32] The temperature dependence of fluorescent emission of the latter compound activated with 2·3% of Eu^{3+} has been studied; its fluorescence is quenched at temperatures above 750 K.[34] The fluorescence lifetime of $NdAl_3(BO_3)_4$ has been measured and the compound suggested as a promising laser material.[147] The europium member of this series shows appreciable non-stoichiometry, deduced by optical spectroscopy and X-ray investigations; not only Al^{3+} sites are occupied by rare-earth ions but other sites as well.[35] Chromium replaces aluminium in $YAl_3(BO_3)_4$ and a luminous spectrum has been recorded of the change.[36]

An n.m.r. investigation of the yttrium compound showed that the $(BO_3)^{3-}$ group had a planar structure.[37] All these borates are classified as belonging to the order of insular borates (i.e. non-ring borate structures with independent polyions).[38] The morphology of $YAl_3(BO_3)_4$ and related rare-earth compounds has been studied.[149–50]

Minerals Containing Aluminium and Boron

Aluminium and boron combine in many ways to form minerals, most of which are very complex; they include the following:

Jeremejevite: Al_2O_3,B_2O_3 (or $Al_6(BO_3)_6(OH)_3$?). (Synthesized.[20, 112])
Sinhalite: $2MgO,Al_2O_3,B_2O_3$. (Synthesized.[144])
Alumoferroascharite: ascharite with B_2O_3 replaced in large part by $(Al,Fe)_2O_3$.
Dumortierite: $(Al,Fe)_7O_3(BO_3)(SiO_4)_3$.
Rhodizite: $CsBe_4B_{12-x}Al_4O_{28}H_2$.
Serendibite: $(Ca,Mg)_5Al_5BSi_3O_{20}$.
Johachidolite: $2Na_2O,CaO,4Al_2O_3,6B_2O_3,5CaF_2,5H_2O$.
Harkerite: $Ca_{48}Mg_{16}Al_3(CO_3)_{18}(BO_3)_{15}(SiO_4)_{12}Cl_2(OH)_6,3H_2O$.
Ettringite: $Ca_6(Si,Al,B)_3(SO_4)_2(O,OH)_{12},12H_2O$.
Tourmaline group: $(Na,Ca)R_3(Al,Fe)_6B_3Si_6O_{27}(O,OH,F)_4$ (R = Mg, Fe^{II}, Fe^{III}, Al, Li, Mn^{II}, Cr).
Axinite group: $2(Fe,Mn)O,2Al_2O_3,4CaO,B_2O_3,4SiO_2H_2O$.
Sapphirine: $9MgO,10(Al,Fe,B)_2O_3,4SiO_2$.
Grandidierite: $2Na_2O,4FeO,8(Fe,Al,B)_2O_3,5SiO_2$.
Kornerupine: $(Mg,Fe^{II},Fe^{III},Al)_{40}(Si,B)_{18}O_{86}$.
Satimolite: $KNa_2Al_4(BO(OH)_2)_6Cl_3,4H_2O$.

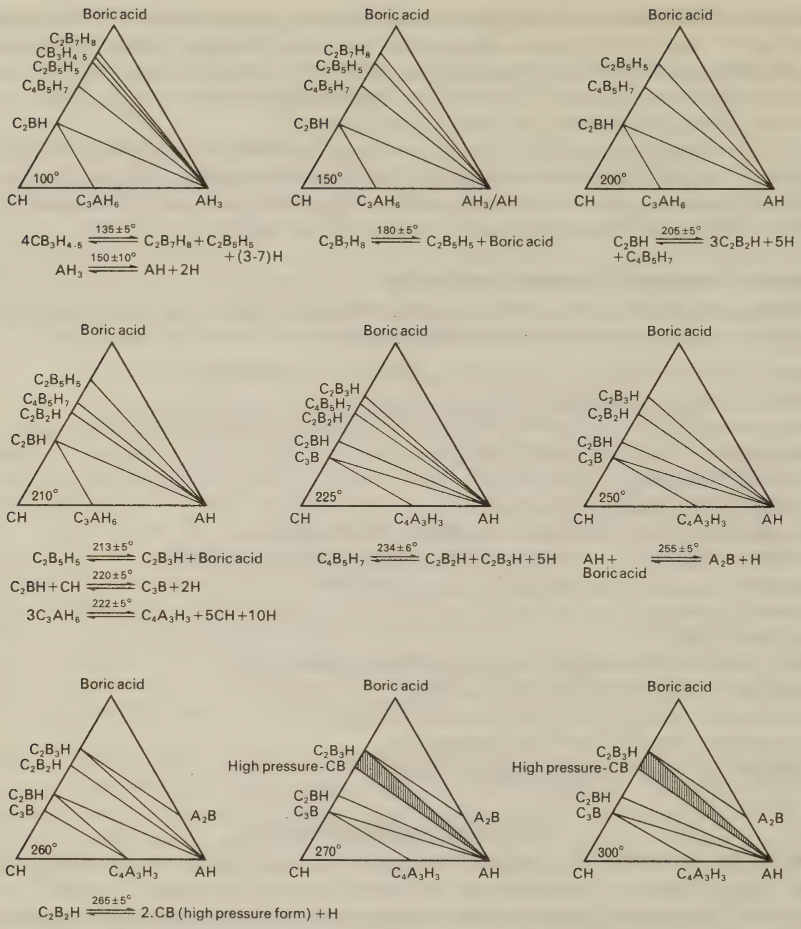
Hydrated Aluminium Borates

Well-defined crystalline hydrated aluminium borates have not yet been synthesized. Metaborates of indeterminate hydration having the general formula Al_2O_3,B_2O_3,nH_2O where $n = 2$ to 6 have been produced by the interaction of 0·2N solution of aluminium nitrate with borax or potassium tetraborate solutions. The composition was determined by the 'inert component' method.[111] Thermal decomposition of the trihydrate has been studied.[145]

It is also possible to produce indeterminate 'aluminium polyborates', xAl_2O_3,yB_2O_3 where $y = 3{\cdot}5$–$27{\cdot}0$ times x.[39] They may be prepared by treating a soluble aluminium salt with a 3·5–27M excess of boric acid or borax. A white precipitate forms as a milky mass which can be filtered and drum-dried.[40] Under other conditions gels are formed by adding strong solutions of borax (20%) to 4·4% solutions of aluminium chloride. Equi-volume addition gives an opalescent gel with a setting time of 5 hours. The addition of slightly less borax gives a transparent gel which takes 10–28 hours to set, and if a 25% excess of borax solution is used an opaque gel is formed which sets instantaneously.[41] Gels may also be formed by adding boric acid or borax to aqueous solutions of basic aluminium chloride $Al(OH)_xCl_{3-x}$.[42] Aluminium oxide gels have the property of removing boron from brines.[43, 45] Other methods of producing aluminium oxide/borate gels are on record.[44] These gels find their use in the preparation of creams and cosmetics, etc.

The mineral *jeremejevite*, which is now accepted as a 'metaborate' containing OH groups has been synthesized recently by hydrothermal methods.[112] $Al_2O_3,3B_2O_3,7H_2O$ and $Al_2O_3,2B_2O_3$ have also been made in this way.[141] The CaO–Al_2O_3–B_2O_3–H_2O system, when studied, showed only hydrated calcium borates and $2Al_2O_3,B_2O_3$ as solid phase borates[132] (see Figs 33 and 34). Double hydroxoborates of aluminium and lithium are known.[137]

Refs. p. 612



$$4CB_3H_{4.5} \xrightleftharpoons{135\pm5^\circ} C_2B_7H_8 + C_2B_5H_5 + (3\text{-}7)H$$

$$AH_3 \xrightleftharpoons{150\pm10^\circ} AH + 2H$$

$$C_2B_7H_8 \xrightleftharpoons{180\pm5^\circ} C_2B_5H_5 + \text{Boric acid}$$

$$C_2BH + C_4B_5H_7 \xrightleftharpoons{205\pm5^\circ} 3C_2B_2H + 5H$$

$$C_2B_5H_5 \xrightleftharpoons{213\pm5^\circ} C_2B_3H + \text{Boric acid}$$

$$C_2BH + CH \xrightleftharpoons{220\pm5^\circ} C_3B + 2H$$

$$3C_3AH_6 \xrightleftharpoons{222\pm5^\circ} C_4A_3H_3 + 5CH + 10H$$

$$C_4B_5H_7 \xrightleftharpoons{234\pm6^\circ} C_2B_2H + C_2B_3H + 5H$$

$$AH + \text{Boric acid} \xrightleftharpoons{255\pm5^\circ} A_2B + H$$

$$C_2B_2H \xrightleftharpoons{265\pm5^\circ} 2.CB\ (\text{high pressure form}) + H$$

FIG. 34.—Phase diagrams (showing compatibility triangles) for the system $CaO–Al_2O_3–B_2O_3–H_2O$

SCANDIUM, YTTRIUM AND THE LANTHANIDE (RARE EARTH) BORATES

Anhydrous Borates

With the great interest in the chemistry of the lanthanides (rare earths) in recent years, the very stable anhydrous lanthanide borates, which may be easily formed from the oxides and boric oxide, usually from a suitable flux, have received their share of attention. Scandium has gained comparatively little notice and there seems to be evidence for the formation of $ScBO_3$ only[123] (see Fig. 35). Yttrium follows the lanthanides very closely in its borate formation; in common with the binary systems of Group II oxides and boric oxide, liquid immiscibility occurs over a large area[45] (see Fig. 36).

The 1:1 borates, written conveniently as $LnBO_3$ (Ln denotes a lanthanide atom), have been investigated most thoroughly. They are stable phases of the $Ln_2O_3–B_2O_3$ systems[46] and are easily formed by heating the correct stoichiometric quantities of the lanthanide oxide with boric oxide at 1200–1400°C[47] or boric acid at 825–1000°C.[115] They melt at temperatures above 1400°C. These borates (Ln = Pr→Lu) are also present as solid phases in the $Na_2O–Ln_2O_3–B_2O_3$ system at 900°C.[48–50] Polymorphism is found in certain of these borates (La, Y, Ce, Pr, Nd, Sm, Lu)

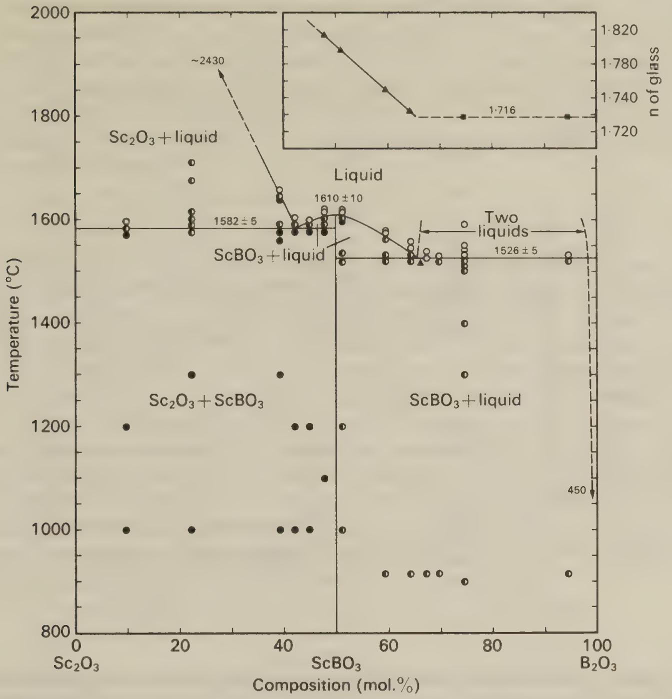


FIG. 35.—Phase diagram for the system Sc_2O_3–B_2O_3.[133] (●) Solid phases only, (◐) solid + liquid phases, (○) one or two liquid phases only, and (▲) chemically analyzed value of gravity-separated Sc_2O_3-rich phase. Equilibrium phase of $ScBO_3$ has calcite-type structure, although a metastable phase of unknown symmetry can be quenched from the liquid. Insert in upper right-hand corner is plot of index of refraction of quenched glass vs. composition

and the relationships of these polymorphs as a function of temperature and ionic radius have been studied.[51–2] The $LnBO_3$ borates (of Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) have a stable vaterite (μ-$CaCO_3$) structure.[47, 51, 53, 116] Lattice constants of the triclinic orthoborates $LnBO_3$ (Ln = Pr, Nd, Sm, Eu, Gd, Tb and Dy) were measured.[172] The polymorphic transitions of $LnBO_3$ borates will be discussed when considering the individual compounds. Unit-cell dimensions, indexed X-ray data and some optical data are available[51]; further studies showed that the unit cells were hexagonal with borate groups parallel to the *c*-axis.[54] Each lanthanide ion is co-ordinated to a distorted cube of 8 oxygen atoms.[54–5] The borate structure of the vaterite type shows a planar T-shaped configuration.[55] A more recent infra-red examination, in the 1500–250 cm^{-1} region, could not be reconciled with three-fold co-ordination of boron, but instead pointed towards four-fold co-ordination in $LnBO_3$ compounds.[56] Lanthanide 1:1 borates obtained from the Na_2O–Ln_2O_3–B_2O_3 system have had their ranges of crystallization established[50] and their thermal stability investigated using D.T.A. techniques; the stability decreases from La→Tb.[49] In certain studies of the phase diagrams of lanthanide borates with lanthanum 1:1 borate, the polymorphic relations of solid solutions of $LnBO_3$ have been investigated by quenching techniques, which show that both aragonite and vaterite-type structures are not stable in the centre of most of the systems.[52] Flux-growth of $LnBO_3$ single crystals from Ln_2O_3–B_2O_3–PbO–MoO_3 (or PbF_2) mixtures has been investigated for a wide range of rare-earth borates.[173] The opalescence of borax beads to which too much of a lanthanide salt is added to obtain the characteristic colour is said to be due to crystallization of the 1:1 borate.[57] Irradiation of the 1:1 borates (of Sm, Eu, Gd, Er) in an argon

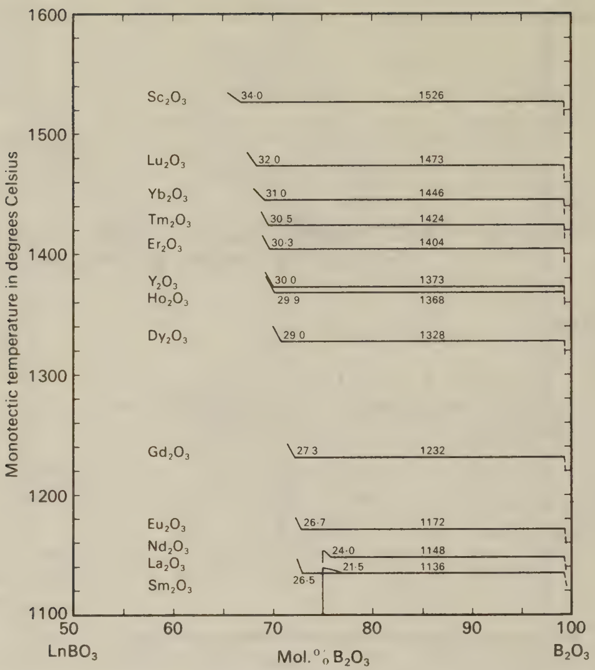


FIG. 36.—Extent of immiscibility and temperature of the monotectonic for lanthanide oxide and boric oxide systems and for the systems Y_2O_3–B_2O_3 and Sc_2O_3–B_2O_3[45]

Small vertical lines on La_2O_3 and Nd_2O_3 systems indicate a $Ln_2O_3,3B_2O_3$ compound, beyond the immiscibility region. In the remaining systems the liquidus rises to the melting point of the $LnBO_3$ compound

atmosphere showed that all but the samarium borate broke down, releasing large quantities of helium.[58]

The formation of 1:2 borates has been postulated in borax bead investigations (of Ce, La, Nd, Pr and Y salts)[57] but no recent evidence exists to confirm their formation. The existence of 1:3 lanthanide borates may explain borax-bead colorations.[57] The properties of 1:3 borates (of Pr, Sm, Eu, Gd, Tb) have been thoroughly investigated; the borates were synthesized by the interaction of the lanthanide oxide and sodium borate at 900°C.[48,50] Further lanthanide 1:3 borates (of La, Ce, Nd), with the same five referred to above, have been synthesized[59] and their properties shown to be very similar, each having the same type of crystal structure.[59] Both X-ray and optical studies were made.[171] 1:3 borates of the heavier lanthanides (Dy → Lu) have not been reported. The 3:1 lanthanide borates have also been prepared from oxides. All crystallize with monoclinic symmetry, the larger ions (La, Pr, Nd) producing structures different from those with smaller lanthanide ions. There is a less radical change between ytterbium and lutecium.[60]

The solubility of lanthanide oxides in the SrO–B_2O_3 system has been studied (for La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb)[61] and mixed borates in monocrystalline form of the formula $Ln_2Sr_3(BO_3)_4$ have been synthesized[62,117] (Ln = Pr, Nb, Gd, Tb, Dy, Ho, Er, and Yb). These double borates have been proved to be isostructural by using infra-red spectroscopy and X-ray phase analysis.[117]

Compounds allied to the latter mixed borates with a general formula $LnX_3(BO_3)_4$, where Ln = rare earth and X = Al, Cr^{III}, Ga^{III}, have been studied. They are formed by reaction of the appropriate oxides in a molybdenum trioxide and potassium sulphate flux (with Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er), from which trigonal crystals with a rhombohedral lattice crystallize.[31] $LaX_3(BO_3)_4$ crystals which have Ln = Yb, Ho, and Er, and X = Al and Cr, are better crystallized from a lead borate $(Pb_3(BO_3)_4$ flux.[33] The lanthanide gallium analogues have been prepared and their structure and fluorescent properties investigated.[63] The majority of these compounds have piezoelectric properties and some (the Y, Sm and Eu compounds with Al) are excited by ultra-violet light to give an excited fluorescent line-width of about 0·9 Å.[31] X-Ray and other crystallographic data have been reported.[33] These '3*d* transition boracites' have been studied especially for their magnetic susceptibilities.[64-5] Properties more specific to the individual elements of the lanthanides follow this more general survey.

Scandium

Single rhombohedral crystals of $ScBO_3$ have been grown from a barium borate flux[66] and a phase equilibrium study for the system Sc_2O_3–B_2O_3 shows the presence of Sc_2O_3,B_2O_3 and the usual liquid immiscibility (Fig. 35).[133] It melts at 1610 ± 10°C.[133] $ScBO_3$ may be prepared in microcrystalline form by heating mixtures of Sc_2O_3, boric acid and alkali metal bicarbonate.[94] It has a calcite structure and lattice dimensions very similar to those of lithium nitrate and magnesium carbonate.[67] Lattice energies have been calculated.[68] Coefficients of thermal expansion were calculated from precise lattice parameters.[161] It is classified together with many of the lanthanide 1:1 borates as being in the order of insular non-ring borates with independent polyions.[38] An impure scandium borate energy transfer was observed from the lowest and from the one-but-lowest excited level of the Ce^{3+} ion to the Tb^{3+} ion.[120] Agreement of the calculated and experimental values of Stark splitting of the Ce^{3+} 4*f* shell with each other revealed a high degree of ionic nature of the compound.[162]

Yttrium

YBO_3 is prepared by the general methods for lanthanide 1:1 borates (*q.v.*). Several crystalline forms exist, polymorphism occurring at high temperatures and giving a stable modification of the μ-calcite (vaterite) type structure.[47, 67, 69] Determinations of interatomic distances show that the metal atoms are located at the centre of a distorted octahedron of oxygen atoms and co-ordinated to one randomly distributed oxygen atom.[55] The lattice energies of the rhombohedral 1:1 borates have been determined.[68] The 1:3 borate is mentioned only in passing in the borax-bead investigations of 1926[57] but is probably formed in the same manner as other lanthanide 1:3 borates. The 3:1 borate has been prepared.[60]

$YAl_3(BO_3)_4$ is one of the three borates of this kind to give ultra-violet excited fluorescence line widths of ~0·9 Å.[31] Activated with 2 or 3% of europium the compound fluoresces more efficiently: the temperature dependence of the fluorescent emission has been measured at temperatures greater than ambient.[34] Cr^{3+} easily replaces Al^{3+} and the electron paramagnetic resonance of the substituted borate has been studied in conjunction with a study of the luminescent spectrum.[71] Recently, a compound of the form $YCr(BO_3)_2$, having a dolomite structure, has been prepared and its crystallographic data determined.[72, 73]

The solubility of $Y_3Al_5O_{12}$ (yttrium aluminium garnet) in PbO–B_2O_3 and PbO–B_2O_3–PbF_2 melts has been investigated, and the method of rapid quenching used to distinguish the stable crystalline regions in the system.[18] The system BaO–$YTaO_4$–B_2O_3 has been used in a comparison with the BaO–$LuTaO_4$–B_2O_3 system in which *perovskite* type compounds are formed.[74]

Lanthanum

The system La_2O_3–B_2O_3 has three solid phases, La_2O_3,B_2O_3, $La_2O_3,3B_2O_3$ and $3La_2O_3,B_2O_3$.[46, 76, 118] By heating the oxides together at 1000–1300°C the 1:1 and 1:3 borates crystallize after about 20 hours. The same authors were also able to produce these two borates from a mixture of lanthanum sulphate and sodium borate at 900–1000°C; they were, however, unable to produce the 3:1 borate in this way.[75] The 3:1 borate can be synthesized[60, 76, 157] but has an incongruent m.p., 1386 ± 5°C.[76] The course of the reaction between pure lanthanum and boric oxides

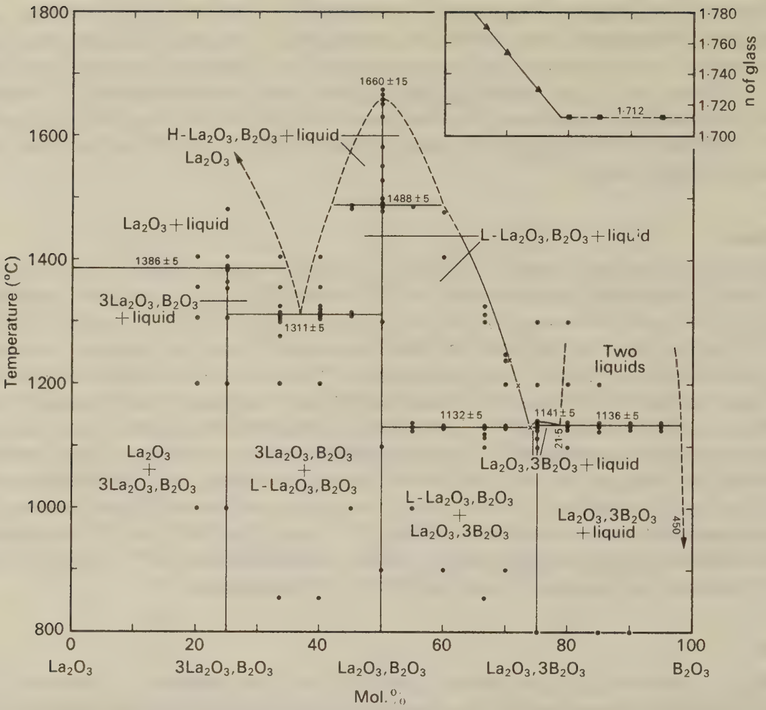


FIG. 37.—Phase diagram for the system La_2O_3–B_2O_3.[76] Solid circles represent compositions and temperatures of study. L=low-temperature polymorph; H=high-temperature polymorph. Inset in upper right-hand corner is plot of index of refraction of quenched glass vs. composition

has been studied by using X-ray and D.T.A. techniques. The binary system is important as a model host for fluorescing systems.[118] La_2O_3,B_2O_3 exists in two polymorphic forms, a low-temperature one which has an aragonite structure and is birefringent[67], and a high-temperature form which has a reversible transition point at 1488 ± 5°C.[51, 76, 159] In a study of the reactions of a number of lanthanide borates with lanthanum 1:1 borate, this high-temperature form was shown to be stable, being a low-symmetry form of calcite-type structure. It was shown, however, that when smaller lanthanide ions (e.g. Lu^{3+}) were added to it, the distortion decreased until $LaLu(BO_3)_2$ was formed when a hexagonal phase was obtained which possibly had the dolomite structure.[52] The 1:1 lanthanum borate has a congruent melting-point of 1600 ± 15°C, one of the highest of all the lanthanide borates.[76] A thermochemical study has been made.[158] X-Ray powder diffraction patterns have been determined for this compound together with other optical characteristics.[77] The effect of the charge on the cation related to cation size has been discussed for lanthanum 1:1 borate in order to explain its structure.[78] It is extremely resistant to water and sodium hydroxide solution (6–12N), even at elevated temperatures; but it is attacked by dilute hydrochloric acid at room temperature.[75]

The 1:3 borate has a congruent melting-point of 1141 ± 5°C.[76] Its crystalline structure has been quite recently determined.[59] This borate in contrast to the 1:1 borate is attacked both by aqueous alkali and by acid.[75]

Glass formation in the system La_2O_3–B_2O_3 has been studied[2], and this system is also found to have a region of immiscibility at 1336 ± 5°C, ranging from almost pure boric oxide to 21·5% La_2O_3[76] (see Fig. 37). In the system La_2O_3–SrO–B_2O_3 a mixed borate of the formula $La_2O_3,SrO,2B_2O_3$ is found as one of the solid phases.[62]

Perovskite compounds are formed in the BaO–$LuTaO_4$–B_2O_3 system, but the comparable lanthanum system shows no such formation.[74] The electrical properties of the TiO_2–La_2O_3–B_2O_3 system have been investigated.[119] A study of the crystal structure of lanthanum cobalt metaborate showed it to be $La_2Co_2[B_6B_4O_{20}]$ and to be composed of infinite $[B_5O_{10}]^{5-}$ chains.[160] (See also p. 643.)

Cerium

Three cerous (Ce^{III}) borates, 1:1, 1:3 and 3:1 are known and are formed by the general methods discussed earlier. The 1:1 cerium borate is also formed by heating the 1:3 borate at 1500°C for 30 hours; it has a density of 5·53.[79] It has two high-temperature modifications, one isostructural with high $LaBO_3$ and the other with high $NdBO_3$.[159] The 1:3 borate is itself alternatively formed by cooling the lower layer of the two-layer melt which is produced when cerous and boric oxides are fused at 1200°C. It has a Ce_2O_3 content of between 2·97 and 60·3%. The optical properties, X-ray data and infra-red spectra of the 1:3 cerium borate are very similar to those of the corresponding compounds of other lanthanides (La, Pr, Nd, Sm, Eu, Gd, and Tb).[59] The addition of half a molecular proportion of cerous oxide to molten boric oxide lowers its density at temperatures below 650°C, but increases the density and surface tension at higher temperatures (700–1200°C).[24, 81]

It is doubtful whether borates of quadrivalent cerium can be formed by solid-phase reaction.[82] Samarium-activated cerium borate fluorescent materials belong to the fluorite type.[83]

A mineral *stillwellite* having an idealized formula $Ce_2O_3,B_2O_3,2SiO_2$ exists.

Praseodymium

The methods of synthesis of 1:1, 1:3 and 3:1 praseodymium borates are described in the general section; there is little else to add that is specific to praseodymium. The mixed borate $Pr_2Sr_3(BO_3)_4$ is also formed by general methods. The green coloration of praseodymium compounds is found in the borax-bead test and is quite specific.[57]

Neodymium

The neodymium 1:1, 1:3 and 3:1 borates are formed by using the previously described general methods (*q.v.*). The 1:1 borate exists in an aragonite form below 1090°C (transition temperature). Its high-temperature form differs from that of the lanthanum compound[51]; it is metastable and is formed by cooling from a phase which is isostructural with the high temperature form of $LaBO_3$.[52, 159] The standard X-ray diffraction powder pattern has been determined, as well as density and refractive indices.[77] The crystal structure of the 1:3 compound has been shown to be monoclinic, containing chains of borate triangles and tetrahedra.[163]

The systems $NdBO_3$–$SmBO_3$ and $NdBO_3$–$LaBO_3$ have been studied and the mixed borate fractions examined.[52] In the SrO–B_2O_3–Nd_2O_3 system, solid phases of Nd_2O_3,B_2O_3 and $Nd_2O_3,3B_2O_3$ are found at 1100°C, and at that temperature it was observed that a separation of liquid phases occurred.[84]

Neodymium salts give a rose-coloured bead in the borax bead test.[57]

The compounds $NdAl_3B_4O_{12}$ and $Nd_2Sr_3(BO_3)_4$ have been formed by the general methods earlier described.

Promethium

The borates of this artificially produced element have been prepared[85] and their chemistry discussed.[86]

Samarium

The general methods of formation have been applied to the three samarium borates, Sm_2O_3,B_2O_3, $Sm_2O_3,3B_2O_3$ and $3Sm_2O_3,B_2O_3$, and a study of the system Sm_2O_3–B_2O_3 shows that each of the three occurs as a solid phase within it.[46]

The samarium 1:1 borate exists in three polymorphic forms[52]:

(a) a form which is structurally similar to the metastable polymorph of $NdBO_3$, and is stable from room temperature to 1065°C;
(b) the high-vaterite form which is stable between 1065° and 1285°C (see also [47]); and
(c) the type isostructural with the high-temperature form of $LaBO_3$, which is stable from 1285°C to the melting point of $SmBO_3$ (see also [51]).

The crystal structure of $Sm(BO_2)_3$, the 1:3 compound but confusingly termed the metaborate, was found to be monoclinic.[164] It consists of $[B_6O_{12}]^{6-}$ radicals (which in turn are composed of two BO_4 tetrahedra and four BO_3 triangles) in chains bounded with Sm polyhedra.

In the $LaBO_3$–$SmBO_3$ and $NdBO_3$–$SmBO_3$ systems the centre portions of the system have the low-temperature polymorph as the stable phase rather than the more normal vaterite type.[52] $SmBO_3$, when irradiated in an argon atmosphere, did not disintegrate with the emission of comparatively large quantities of helium, whereas other lanthanide borates (Eu, Gd, Dy and Er) did so under identical conditions.[58]

The mixed borate $SmAl_3(BO_3)_4$ is one of the three lanthanide (Y, Sm, Eu) aluminium borates which show an ultra-violet excited fluorescence line width of 0·9 Å.[31] The properties of $SmCr_3(BO_3)_4$ were also studied.[31]

A study of the SrO–B_2O_3–Sm_2O_3 system showed the presence of $Sm_2O_3,3B_2O_3$ and $SmCr_3(BO_3)_4$ as solid phases.[61] The Sm_2O_3–B_2O_3–CoO system has been studied and the crystal structure and infra-red spectrum of $SmCo(BO_2)_5$ determined.[165–7] It is orthorhombic, d(expl.) = 4·70 and m.p. = 1080°C.

Evidence exists for the formation of a borate of bivalent samarium by metathetical reaction with samarous chloride $SmCl_2$. The product formed orange-red crystals.[87]

Europium

Few specific properties of europium borates are reported. The three usual borates (1:1, 1:3, and 3:1) are formed. Eu_2O_3,B_2O_3 has a stable vaterite structure, and no polymorphism is found; it has the lowest m.p., 1540°C, of all the 1:1 lanthanide borates.[51] It has the same ultra-violet-excited fluorescence spectrum band-width as the yttrium and samarium compounds.[31] Sintering Eu_2O_3 with B_2O_3 afforded Eu_2O_3,B_2O_3 and $Eu_2O_3,2B_2O_3$.[168–9] Complexes with hydroxycarboxylic acids were prepared. Eu_2O_3,B_2O_3, although less stable to irradiation than the corresponding samarium compound[58], absorbs neutrons without altering its physical form (e.g. compacted powder).[88] No ternary borates are found in the SrO–Eu_2O_3–B_2O_3 system. The binary solid phases are $Eu_2O_3B_2O_3$ and $Eu_2O_3,3B_2O_3$.

Gadolinium

Gadolinium is a very regular member of the lanthanides as far as its borates are concerned, and all general methods for their formation are applicable. Some work has been done on $GdBO_3$ as a phosphor, doped with 2–3% of europium. It has been shown that this phosphor shows emission spectra characteristic of europium, indicating that energy absorbed by gadolinium can be transferred to europium ions.[89] The temperature dependence of the fluorescent emission of this phosphor has been studied.[34] The crystal parameters of the 1:3 gadolinium borate have been derived; it is monoclinic.[121] Its structure is similar to the corresponding samarium compound. [164, 170]

Terbium

General methods of formation are used for terbium borates. The 1:1 borate shows no polymorphism.[51] A study of terbium borates obtained from the Na_2O–Tb_2O_3–B_2O_3 system shows that they are the least thermally stable of lanthanide borates.[49] The 1:3 terbium borate has a rhombic structure; its crystal parameters have been studied.[121]

Dysprosium

This element forms the 1:1 and 3:1 borates, but no specific properties are reported. Its borates and mixed borates found are mentioned in the general section above. Metaborates of Dy to Lu can be synthesized by reaction of the rare-earth oxide with molten sodium borate.[170]

Holmium

As with dysprosium, there is little specific to be said about the borates of this element, although the SrO–Ho_2O_3–B_2O_3 system has been studied in detail and the compounds Ho_2O_3,B_2O_3, $Ho_2O_3,3SrO,2B_2O_3$ and $2SrO,B_2O_3$ are reported.[62] The 1:3 borate has not been reported.

Erbium, Thulium and Ytterbium

There is no record of the formation of the 1:3 borates. However, ytterbium borate is on record as having a calcite structure.[70]

Lutetium

The 1:1 and 3:1 borates are formed by general methods, but there is no record of the 1:3 compound. After the series of 1:1 borates (Eu → Yb) in which no polymorphism occurred, lutetium follows the properties of the lanthanides of lower atomic number and has a calcite structure below 1310°C and a vaterite structure above that temperature.[51] Interatomic distances and other crystallographic and optical data have been determined for Lu_2O_3,B_2O_3. From these data, it has been shown that the metal atoms are each at the centre of a distorted octahedron of oxygen atoms, and co-ordinated to one randomly distributed oxygen.[55] If lutetium replaces lanthanum progressively in La_2O_3,B_2O_3, the distorted calcite type structure of the latter becomes less distorted until the mixed compound $La_2O_3,Lu_2O_3,2B_2O_3$ is formed, which is a hexagonal phase possibly having a dolomite structure.[52]

In the system BaO–$LuTaO_4$–B_2O_3 there is a *perovskite* primary region phase consisting of crystals analysing $Ba_{0\cdot925}Lu_{0\cdot550}Ta_{0\cdot500}O_3$. This system is compared with the corresponding systems in which yttrium replaces lutetium.[74]

Hydrated Lanthanide Borates

Hydrated borates of the lanthanides and yttrium (with the exception of Er, Tm and Lu) have been prepared by adding 0·1N borax solution to lanthanide chloride solution at pH 6·5–6·9. The centrifuged precipitate, washed with 2% sodium chloride solution, is dried at 60°C to give a dry product analysing at $Ln_2O_3,3B_2O_3,6H_2O$. Tetrahydrates (Nd, Gd, Dy and Ho) were obtained by drying at 80°C. The solubilities of the borates at pH 6 and 25°C are tabulated and show a decrease (La → Gd) and then an increase (Dy → Yb).[90] The only other crystalline hydrated lanthanide borate on record is the mineral *braitschite*, which contains most of the lanthanides to varying extents, calcium as a major constituent and sodium as a minor constituent.[110]

A cerium borate gel is formed by the reaction of borax on cerium ammonium nitrate.[91] The surface hydration of this gel, by using derived Hatchek's equation, is about 80%, and this agrees with values obtained from syneresis and thixotropy determinations.[92]

A method of quantitative precipitation of gadolinium as metaborate has been used to determine small quantities of gadolinium.[93] Lanthanum has also been determined as the 1:3 borate by using conductimetric methods.[109]

GALLIUM AND INDIUM BORATES

Gallium and indium borates, $GaBO_3$ and $InBO_3$, are known, as is the metaborate $InBO_2$ whose spectra in solid and vapour states have been studied.[155] High-pressure methods were necessary for the synthesis of $GaBO_3$.[151] $InBO_3$ may conveniently be prepared in microcrystalline power form by heating In_2O_3, boric acid and alkali metal bicarbonate at 700°C for 2–3 days.[94] Spectroscopic properties of the orthoborate ion in the $InBO_3$ single crystal have been measured.[125] In structure the indium borate $InBO_3$ is quite comparable with many of the lanthanide 1:1 borates. The rhombohedral crystals[68] have an aragonite-type optical behaviour[67, 78] and exhibit no polymorphism.[51] Its lattice energy has been calculated[68] and the force constants of the borate ion determined.[96] The infra-red absorption spectrum has been recorded.[97] $InBO_3$ activated with small percentages of europium has a superior luminous efficiency to similarly activated lanthanide borates.[98] No mixed borates of indium are recorded, but gallium forms a series of anhydrous compounds of the general formula $Ln_2O_3,3Ga_2O_3,4B_2O_3$ where Ln = lanthanide.[63] A range of lithium galloborates was found in the $Li_2O–B_2O_3–Ga_2O_3$ system[124, 126–8], and similar sodium compounds in the $Na_2O–B_2O_3–Ga_2O_3$ system.[122, 129–31] Mixed gallium–bismuth and gallium–iron borates have been made.[95] There are no recorded hydrated borates of gallium and indium and no anhydrous borates of lower-valent gallium or indium.

THALLIUM BORATES

In the formation of thallium borates, anhydrous or hydrated, the thallium appears to be restricted to its most stable (monovalent) form.

Anhydrous Thallium Borates

The earlier edition (Mellor, V, 102) quotes the existence of the 1:1, 2:1 and 3:1 borates. Later work added the 1:2 and 1:4 borates to these as well as substantiated thallium borates[99, 100], but found no evidence for the 2:1 borate. Further work showed the existence of the 1:3, 1:5 and 1:9 borates, with still no evidence of the 2:1 borate

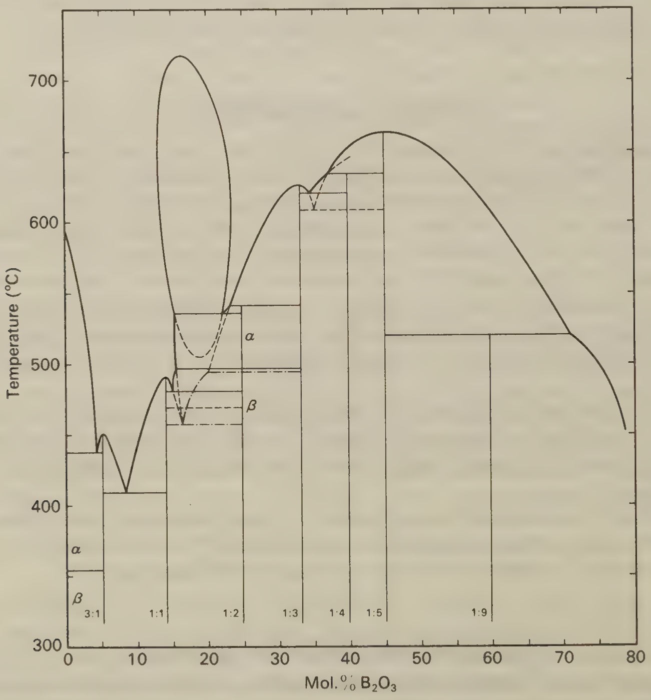


FIG. 38.—Phase diagram of the system $Tl_2O–B_2O_3$[134]

in the system[134] (see Fig. 38). The 1:2 borate is quoted as existing in three allotropic forms.[126] The 1:1 compound has been prepared at high pressure and a calcite structure described.[151] The infra-red spectra[155] and mass spectra[156] of thallium metaborate, $TlBO_2$, vapour have been studied.

The inter-reticular distances and intensities have been measured from the X-ray patterns of all the thallium borates including the three (α-, β-, and γ-) forms of the 1:2 borate.[99,134] A detailed study of the α-form confirmed the presence of a metastable liquidus branch JD in the phase diagram (Fig. 38). Unlike the borates of Group II and the lanthanides, etc., thallous and boric oxides are miscible in all proportions, no double liquid layers being formed.[101] An investigation of the Tl_2O–B_2O_3 system showed that the cations are present in pairs, as with caesium glasses, and their distribution is subject to fairly rigid restriction, indicating a certain ionic order.[102] Lattice parameters of the orthorhombic crystals Tl_3BO_5 and TlB_5O_8 have been determined.[152] Tl_3BO_3 is hexagonal.[153] The stereochemical role of the lone doublet of thallium (I) in the thallium borate structure has been discussed.[154] A new type of double oxide, $TlNbB_2O_8$, has been synthesized and its structure investigated.[80] The electrical conductivity of Tl_2O–B_2O_3 glasses have been studied in the range 20–75 wt.-% Tl_2O.[103]

Thallium also forms hygroscopic, colourless crystals of the type $M(B(SO_4)_2)$ by reaction of thallous sulphate with 2 molecules of boric acid and 6 molecules of sulphur trioxide[104] (cf. borates of alkali metals and silver).

Hydrated Thallium Borates

Buchtala produced the following series of hydrated thallous borates: 1:1:1, 1:2:2, 1:3:3, 1:4:4, 1:5:8 and 1:6:7 (see Mellor, V, p. 103). This work was repeated by two Italian workers in 1938 using slightly different methods and obtaining somewhat different results.[105] They were unable to produce Tl_2O,B_2O_3,H_2O by evaporation of an aqueous solution of the borate, but did obtain it by double decomposition of sodium metaborate with an aqueous solution of thallous nitrate. The 1:2:2 compound was formed by the older method as well as the straightforward double decomposition reaction, this time using borax and thallous nitrate. By following the procedure of Buchtala for the formation of the 1:3:3 borate but extracting with boiling water both 1:3:3 and the 1:2:2 compounds were obtained. The 1:4:4 and 1:6:6 compounds were formed by following the Buchtala method for producing the former. Instead of yielding a mixture of 1:3:3 and 1:5:8, which is obtained by extracting with cold water, extraction with boiling water gave the 1:5:5 alone. $Tl_2O,6B_2O_3,6H_2O$ was formed by using Buchtala's method for the formation of $Tl_2O,6B_2O_3,7H_2O$. This interesting series of compounds of the general formula $Tl_2O,x(B_2O_3,H_2O)$, where $x=$ 1–6, was explained by the more recent workers by the reluctance of the Tl^+ ion to hydrate, leaving the hydration to build up over the series at the same rate as the boric oxide.[105]

In a more recent investigation of thallium borates, this series of borates was not found in the Tl_2O–B_2O_3–H_2O system at 30°C, the compounds isolated being $Tl_2O,5B_2O_3,8H_2O$, $Tl_2O,2B_2O_3,3H_2O$, Tl_2O,B_2O_3,nH_2O and $3Tl_2O,B_2O_3,xH_2O$. These compounds were found by thermogravimetric and radio-crystallographic means and identified by crystallographic examination. The last two borates were also prepared from solutions of thallous carbonate and boric acid. $Tl_2O,2B_2O_3,3H_2O$ dehydrates to $2H_2O$ at 140°C and loses another molecule of water at 185°C; the anhydrous form is obtained at 280°C.[106]

Further study of the Tl_2O–B_2O_3–H_2O system[107] shows the presence of $2Tl_2O,5B_2O_3,5H_2O$, which is apparently a stable hydrate up to 100°C.

The interplanar spacings have been calculated from X-ray powder diagrams for 1:2:1, 1:2:2, 1:2:6 and 1:5:8 hydrates.[100]

The restricted system $Tl_2O,2B_2O_3$–H_2O has been studied.[108]

The information on thallium borate hydrates is still in a somewhat confused state, which may be clarified by current work in this field.

Refs. p. 612

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BORATES OF GROUP IV

BORATES CONTAINING SILICON

Hardly surprisingly, silicon does not combine with boric oxide to form silicon borates, as they are both weak acidic oxides in the classical sense. They do, however, combine in the presence of alkaline oxides to give complex series of metal borosilicates. These will not be discussed here and reference to them will be found included with the metal borate in question. In the field of glass technology (*q.v.*) the formation of glasses principally containing silica and boric oxide as a major constituent, together with small percentages of alkali-metal oxides and alumina, led to the development of the industry producing '*Pyrex*' (Registered Trade Mark) brand chemical and heat-resistant borosilicate glasses. These glasses have very low coefficients of expansion (comparable to that of fused silica) but have melting points in the 1000°C region (compared with 1700°C for silica).[10]

Although no silicon borates are formed, an appreciable volume of work has been directed towards proving this and determining whether or not liquid immiscibility is to be found in the system SiO_2–B_2O_3. Using the phase diagram and a simple solution model a sub-liquidus miscibility gap was estimated for the SiO_2–B_2O_3 system. Gradient-furnace heat-treatments of selected compositions gave results corresponding closely with the predicted co-existence boundary, which showed a consolute temperature of 520°; this boundary was flat and symmetrical and extended across the complete binary[11] (see Fig. 39). This recent work seems to settle the controversy concerning miscibility or immiscibility in the system, but it does not confirm the hypothesis that compounds could exist in it.[12] The formation of two liquid phases was postulated previously, but for temperatures above the liquidus[13]; other workers disagreed.[14–16, 23] Viscosity minima are shown at 5% SiO_2 at 530°C, 5%

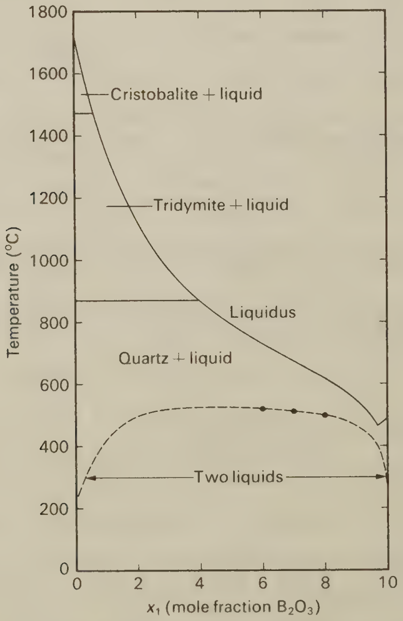


FIG. 39.—Phase diagram for the system B_2O_3–SiO_2

Solid line represents stable equilibrium; dashed line, calculated metastable two-liquid coexistence boundary. Points (●) represent observed temperatures for onset of miscibility and 12% at 630°C and none at 800°C.[18] Breaks are shown in all curves relating specific volumes, expansion, and freezing points to composition, at about the same molar percentage of B_2O_3, i.e. 42%.[19]

The following ternary or pseudo-ternary systems have been studied:

Na_2O–B_2O_3–SiO_2 (refs. 20, 21, 22)
$Na_2O,4B_2O_3$–Li_2O,SiO_2,SiO_2 (ref. 1)
CaO–B_2O_3–SiO_2 (refs. 23, 24)
BaO–B_2O_3–SiO_2 (refs. 25, 26)
ZnO–B_2O_3–SiO_2 (ref. 27)
PbO–B_2O_3–SiO_2 (refs. 28, 29, 95)
Li_2O–$(Al_2O_3$–$SiO_2)B_2O_3$ (ref. 28)
PbO–$(Al_2O_3$–$SiO_2)B_2O_3$ (ref. 28)

Compound formation in these systems is mentioned in the sections dealing with the appropriate metal borate concerned.

TITANIUM BORATES

There is, as yet, no evidence for the formation of hydrated titanium borates. A few minerals exist which contain titanium but they are not hydrated, e.g. *warwickite* $3(Mg,Fe)O,TiO_2,B_2O_3$ and *titantourmaline* where (R is mainly Ti in the general formula for tourmaline), $(Na,Ca)R_3(Al,Fe)_6B_3Si_6O_{27}(O,OH,F)_4$.

Titanous Borates

The simple 1:1 titanous borate ($TiBO_3$) has been formed by gas-phase transport reactions in a sealed quartz tube at 900°C for 48 hours (see *boracites*, ref. 45).[30] The borate was formed in hexagonal platelets, red-brown in transmitted light and greenish dark brown in reflected light. $CrBO_3$ and VBO_3 have also been formed in the same way. Only small quantities of these compounds have been formed, apparently, insufficient for chemical analysis. Physical analytical methods show that the lattice spacings are very similar to those of $Fe_{1-x}M_xBO_3$ where M = Ga, Cr or Ti.[31] These iron/titanium borates are isostructural with aragonite (cf. lanthanide borates) and are formed by reaction in a flux (comprising the oxides Ti_2O_3, Bi_2O_3, and B_2O_3 in the molecular ratio 1:1:5) at 1200°C and annealing for some days at 900°C.[31]

A double borate $2MgO,Ti_2O_3,B_2O_3$ is also formed, in this case by electrolysis of the oxides in a molten-salt bath. Its crystallographic parameters have been determined.[32]

Titanic Borates

No simple titanic borates have been reported, but electrical properties of the TiO_2–B_2O_3 system have been investigated.[3] Titanium dioxide is soluble in boric oxide to the extent of 4·81 wt.-% at 1200°C[33] and in molten borax 10·86 wt.-% at 900°C.[34] In the case of titanium dioxide in borax the solubilities have been determined over the range 730–972°C and compared with the solubility of rutile in potassium and lithium tetraborates.[35] Titanium dioxide only can be crystallized from these melts. However, the solubility does not agree with the Schroder equation for non-reactive solubility, thus indicating a vigorous chemical reaction.[34]

By heating titanium dioxide in hydrogen at high pressures until 20–80% of the oxygen is lost as water, and then heating the oxygen deficient oxide with boron it can be incorporated into the lattice to give a compound which can be written $TiOB_{0\cdot4}$. This product forms part of a mixture suggested as a high-temperature wear-resistant material.[35]

The only true titanic borate known is TiO_2,BaO,B_2O_3 or $TiBa(BO_3)_2$ which has a dolomite structure and forms a series of solid solutions with another member of the family, $SnBa(BO_3)_2$. The stability of this compound and others of the series has been discussed.[2,37] The BaO–TiO_2–B_2O_3 system has been examined by quick cooling in water, natural cooling in air, natural cooling in a furnace and slow cooling in a furnace.[38] A mixed nickel titanium borate, $TiO_2,5NiO,B_2O_3$, has been prepared and found by single crystal X-ray analysis to be orthorhombic, as the mineral ludwigite.[124]

The following systems have been studied with no reference to a borate containing titanium as a solid phase:

$PbO–BaO–B_2O_3–TiO_2$ (ref. 39)
$PbTiO_3–PbZrO_3–(50\%\ PbO+50\%\ B_2O_3)$ (ref. 40)
$PbNb_2O_6–PbTiO_3–(50\%\ PbO+50\%\ B_2O_3)$ (ref. 41) (see Fig. 39)
M_2O,B_2O_3+(equimolar $M_2O,6TiO_2/M_2O,2B_2O_3$) ($M = K, Na$) (ref. 123)

No glass formation was found in any of the following systems[42]:

$BeO–TiO_2–B_2O_3$
$Al_2O_3–TiO_2–B_2O_3$
$ZrO_2–TiO_2–B_2O_3$
$Ta_2O_5–TiO_2–B_2O_3$
$WO_3–TiO_2–B_2O_3$

Crystallization in the systems

$PbO–B_2O_3–TiO_2$

and

$PbO–TiO_2–SiO_2–B_2O_3$

has been studied.[43]

It is also recorded that undefined anhydrous titanium borates may also be formed by mixing boric acid with titanium dioxide or the metal at 1300–1450°C, droplets of the molten borate being collected in a container charged with ethoxysilane.[17] Borates of chromium, nickel, copper, zinc, zirconium, tin, tungsten and lead are also recorded as being produced in the above manner.

ZIRCONIUM BORATES

Anhydrous Zirconium Borates

There is no evidence for the formation of a simple zirconium borate; it is, however, reported that a hydrated zirconium borate $ZrO_2,B_2O_3,3H_2O$ may be dehydrated at 400°C to give ZrO_2,B_2O_3 but with 2–3% decomposition at 500–600°C.[44] It is unlikely that this anhydrous compound is sufficiently well-characterized to be defined as a true borate.

Zirconia is soluble to the extent of 1·57% in molten boric oxide at 1200°C[33] but does not react.[34] It is insoluble in fused borax (Mellor, V, 106).

Two crystalline ternary zirconium borates have been reported. A lead borate PbO,ZrO_2,B_2O_3 has been obtained as a solid phase in the system $PbZrO_3–(50\%\ PbO+50\%\ B_2O_3)$[45] and in the more complex system $PbTiO_3–PbZrO_3–(50\%\ PbO+50\%\ B_2O_3)$ at 1000°C, the other phases being a glass and $Pb(Ti,Zr)O_3$. Another method of preparation and the properties of PbO,ZrO_2,B_2O_3 have been described.[9] The other borate, BaO,ZrO_2,B_2O_3, has been patented as a good pigment (refractive index 1·77) for aqueous emulsion paints. It is formed by sintering stoichiometric quantities of barium carbonate, zirconium dioxide and boric acid at 1050°C.[46] The latter and other borates of the general formula $M^{II}Zr(BO_3)_2$ (M^{II} = Ca, Sr, Ba, Cd) crystallize from molten solutions.[2]

Crystallization in the systems $Na_2O–B_2O_3–ZrO_2–SiO_2$ and $Na_2O–Al_2O_3–ZrO_2–SiO_2$ has been studied[47] and the former system shown to be capable of supporting a large percentage (15–20%) of zirconia[48] but still retaining its chemical resistance and clarity. No glass formation was found in the following systems[42]:

$BeO–ZrO_2–B_2O_3$
$Al_2O_3–ZrO_2–B_2O_3$
$TiO_2–ZrO_2–B_2O_3$
$Ta_2O_5–ZrO_2–B_2O_3$
$WO_3–ZrO_2–B_2O_3$

Hydrated Zirconium Borates

A hydrated zirconium borate has recently been formed and defined as ZrO_2,B_2O_3,$3H_2O$[44], but as gels have been persistently formed in the past, it is advisable to await confirmation of it as a definite crystalline compound. It is produced by the reaction of one mole of $ZrO(NO_3)_2$,$2H_2O$ and two moles of borax in aqueous solution. It is reported that it loses 2 molecules of water at 200°C and that the last traces of water are lost by 400°C.[44] A gelatinous precipitate, presumably a basic zirconium borate, is formed at the same pH as the hydroxide, but the precipitation is delayed.[49] According to the concentration of electrolyte in the system a stable gel or a gelatinous precipitate is formed. An excess of electrolyte favours the latter.[50] The gel formed in the presence of moderate quantities of electrolyte has a $ZrO_2:B_2O_3$ ratio of 3:2.[50] Rate of syneresis is related to the quantity of added electrolytes and the addition of alcohols to the system.[51] In the case of added electrolytes, changes in depolarization, intensity of transversely scattered light and opacity have been studied showing that particles increase in size during and after gelation and are probably disc-shaped. Anisotropy increases only slightly under these conditions.[52] Among other proportions, the extinction coefficient of zirconium borate gels has been determined.[7]

More recently, the compound $ZrOB_4O_7$,$4H_2O$ was obtained when $ZrOCl_2$ was treated with a saturated solution of H_3BO_3 at 30°C and pH = 4.[125] It is converted on storage to $Zr(OH)_2B_4O_7$,$2{\cdot}5H_2O$ but on heating to 1,000°C loses all four molecules of water. Later work by the same authors showed that a mixture of ZrO_2 and B_2O_3 resulted from heating to below 800°C, and that zirconium tetraborate hydrolysed to zirconia hydrate.[126] The adsorption of borate ions onto zirconium hydroxide has been studied by others.[160]

HAFNIUM BORATES

Hafnium borates do not seem to have been prepared.

THORIUM BORATES

An amorphous ThB_2O_5 gel was formed by the reaction of aqueous solutions of thorium nitrate and borax, and could be transformed to crystalline material on heating to elevated temperatures.[151] Large single crystals of ThB_2O_5 were obtained by reacting the parent oxides at 1300°C. Since neither ZrO_2 nor UO_2 form crystalline compounds with B_2O_3 in this way, a basis for separation is suggested.[151] ThB_2O_5 was found by other workers to be an intermediate phase in the $ThO_2–B_2O_3$ system.[152] It is monoclinic and melts at 1483 ± 5°C to form two immiscible liquids, one containing about 98 mol-% B_2O_3 and melting below 325°C and the other with 18–20 mol-% B_2O_3 and melting at just under 1483°C. The $ThO_2–B_2O_3$ system has been studied for areas of glass formation.[153] Earlier work had indicated a solubility of thoria in boric oxide of only 0·57% at 1200°.[154]

Hydrated thorium borates have not been characterized, but sols and gels have been studied.[155–6] The coagulum of a sol obtained by a cataphoretic method from borax and thorium nitrate had the composition $4ThO_2$,$Th_3(BO_3)_4$. Electrolytes coagulated the sol very easily, but glucose and glycerol had a peptizing effect. Optical studies of the gels showed that the particles continuously increase in size during and after gelation, although the anisotropy increases only slightly, and are probably disc-shaped.[157] Early studies had shown that precipitation of 'thorium borate' from solution was delayed, as with the corresponding zirconium situation.[158]

GERMANIUM BORATES

No germanium borates are known. A phase diagram for the GeO_2–B_2O_3 system has been prepared.[56] Glasses are formed by all compositions of the two oxides[57], and the properties of these glasses have been studied.[58, 59]

The polarographic behaviour of germanium dioxide in molten borax at 820°C was studied, and well-developed waves obtained to which $i_d = kN$ applied (where N = molar fraction of GeO_2).[60] Germanium has been obtained by electrode position from germania dissolved in molten borax.[61]

The expansion coefficients of the Na_2O–GeO_2–B_2O_3 system have been investigated[58] and the effect of adding germania to alumino-borate melts studied.[62] The crystal structure of lithium borogermanate, $Li_2O,B_2O_3,2GeO_2$ has been determined.[127]

TIN BORATES

Anhydrous Tin Borates

There is no record of the formation of simple tin borates of either valency state, but mixed borates such as *nordenskiöldine* (CaO,SnO_2,B_2O_3) and others of the same general formula (MO,SnO_2,B_2O_3) have been prepared and quite thoroughly studied. Ouvrard first synthesized the latter compounds (Mellor, V, 105) by passing stannic chloride vapour over a red-hot borate, or hydrogen chloride gas over a mixture of calcium 'tetraborate' and stannic oxide. Later syntheses were carried out hydrothermally in an autoclave by the action of stannic oxide and borax, on calcium oxide or carbonate in the case of nordenskiöldine or the appropriate oxide or carbonate in the other cases.[63] Borates of this form where M = Mg, Ca, Sr, Ba, Cd, Mn, Fe, Co, Ni have thus been prepared.[2, 37, 63] and all appear to have a dolomite-type structure.[37, 64, 65] Study of the structures suggests that the positions of the oxygens in MgO,SnO_2,B_2O_3 and SrO,SnO_2,B_2O_3 provides evidence for a small rotation of the $(BO_3)^{3-}$ triangles with respect to the ideal positions when the radius of M increases ($Mg \rightarrow Sr$).[65] The barium compound BaO,SnO_2,B_2O_3 forms a series of solid solutions with the corresponding titanium compound BaO,TiO_2,B_2O_3.[37] The conditions for the formation of the mineral *hulsite* $(Fe,Ca,Mg)_4(Fe,Sn)_2$-B_2O_{10} have been determined[5] and its high-temperature formation discussed.[54]

Well-developed polarographic waves are formed for stannic oxide in molten borax at 820°C[60], but a degree of chemical polarization occurs during electrolysis.[66] Stannic oxide is soluble in boric oxide at 1200°C to the extent of 0·82%.[33]

Trimethyltin metaborate, $(CH_3)_3SnBO_2$, is formed by the reaction of silver metaborate with trimethyltin bromide.[129] Properties, including spectra, have been recorded.

Hydrated Tin Borates

As with zirconium and hafnium, stannic borate gels are known. They are formed by mixing tin chloride or nitrate with sodium or potassium borate. The empirical formula $Sn_3(BO_3)_4$ has been assigned to the gel.[67] A gel (30% solids) formed by mixing 2 moles of powdered borax with 1 mole of $SnCl_4,5H_2O$ in aqueous solution and adjusting the pH to neutral is recommended as a colour-stability improver for addition to soaps (0·003–2%).[68] The $SnCl_2$–$Na_2B_4O_7$–H_2O system was studied and the composition of solid phases confirmed by infra-red spectra and thermogravimetric analysis.[128]

A patent describes the formation of copper, tin and zinc borates obtained by treating the appropriate metal with an aqueous solution of boric acid in the presence of ammonia and air or oxygen. They are recommended as insecticides or anticryptogamics.[69]

LEAD BORATES

Lead borates have been the most extensively studied borates of Group IV, partly because of the common use of lead oxide and boric oxide in glass formulations, but also because no other Group IV metal reacts so variously with boric oxide. The first edition of this treatise does not identify exactly any anhydrous lead borates and as far as hydrated lead borates are concerned, comment was 'a few lead borates have been reported as precipitates formed by double decomposition, but so long as chemical analyses alone are available there will be doubts concerning the chemical individuality of the observed products' (Mellor, V, 106). This statement has proved to be true, not only for hydrated compounds but also for the anhydrous lead borates and other borates. Methods of identification using X-ray powder techniques and other physicochemical methods have certainly rationalized the chemistry of these compounds.

ANHYDROUS LEAD BORATES

The first investigation of the $PbO–B_2O_3$ system[70] to determine the areas of existence of binary lead borates was carried out from '. . . data obtained from heating curves and microscopic examination without apparently holding compositions at crystallizing temperatures for prolonged periods of time'.[71] Of the solid phases found by the first workers, PbO,B_2O_3, $PbO,2B_2O_3$, $2PbO,5B_2O_3$ and $PbO,3B_2O_3$, only the 1:2 borate was found in the system using the more sophisticated quenching method combined with identification of the crystalline phases by optical methods. Investigators using this method[71] found, as well as $PbO,2B_2O_3$, the following borates:

$5PbO,4B_2O_3$
α- and β-$2PbO,B_2O_3$ (polymorphs)
α- and β-$4PbO,B_2O_3$ (polymorphs) (see Fig. 40).

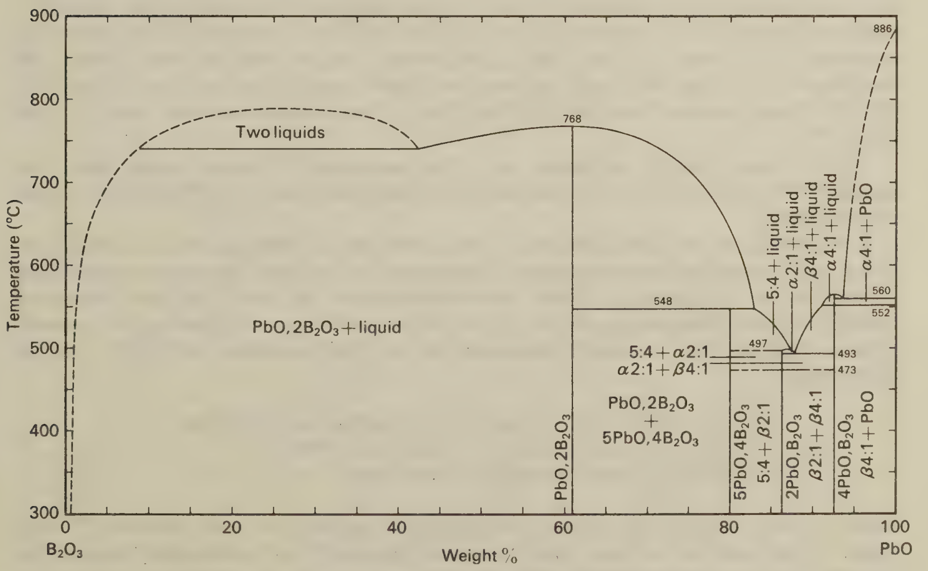


FIG. 40.—Phase diagram for the system $PbO–B_2O_3$[71]

In a later study of this type, in which breaks in a dielectric constant curve in addition to changes in absorption spectra were observed, the presence of three crystalline compounds was indicated: $PbO,2B_2O_3$, $5PbO,4B_2O_3$ and $2PbO,B_2O_3$.[132] In 1967 the section of the system $PbO,2B_2O_3$–$5PbO,4B_2O_3$ was studied in greater detail, isolating three previously unidentified metastable monotropes, α-, β- and γ-PbO,B_2O_3 and a further compound, $9PbO,8B_2O_3$.[72] This area was said by the former workers to be an area in which metastable phases could exist. The phase diagram shows an area of two liquid phases in equilibrium, characteristic of so many borate systems, and the indications are that in the 1–19 mol.-% B_2O_3 range, metastable subliquidus and subsolidus two-liquid regions are likely to exist.[73] In a later study of the miscibility gap in the PbO–B_2O_3 system, the temperature of phase separation was described as a function of composition.[131] The two phases were given as B_2O_3 and $PbO,4B_2O_3$ The transitions can take place in metastable equilibrium with the crystalline phase. Melts in the PbO–B_2O_3 system crystallize if the molecular percentage of PbO is over 70; if the mol.-% PbO is less than 21, milky glasses are obtained as a result of layering.[74, 75] The tendency to supercool has been investigated.[134]

Decomposition in the systems PbO–B_2O_3 and PbO–B_2O_3–SiO_2 has been studied by conductimetric methods[76] and the electrical conductivity of PbO–B_2O_3 melts has been measured in detail.[77] X-Ray diffraction studies of melts in the $PbO:B_2O_3$ ratio range of 4·0 → 0·33 showed that Pb–O bonds become more ionic by fusion of the crystalline borates and by increasing boric oxide concentrations[78]; but only in the case of β-$4PbO,B_2O_3$ does the configuration of Pb–O alter.[79] The formation of glass at the abnormally high PbO concentration of 94% was explained in this way.[78] The solid phases of the PbO–B_2O_3 system have been identified by X-ray diffraction techniques.[80] A thermodynamic study of PbO–B_2O_3 melts has been made.[55] Activities, partial molar enthalpies, entropies and free energies of the PbO–B_2O_3 system were obtained from e.m.f. measurements in cells at 750–1050°C.[133]

The PbO–B_2O_3 system was studied by differential thermal analysis, as were the more complex systems[43]:

$$PbO\text{–}B_2O_3\text{–}TiO_2$$
$$PbO\text{–}TiO_2\text{–}SiO_2\text{–}B_2O_3$$
$$PbO\text{–}ZnO\text{–}B_2O_3.$$

The structure of PbO–B_2O_3 glasses has been investigated and several types of BO_3 units shown to be present.[79] At low percentages of PbO, BO_4 units and Pb^{2+} ions are common but are gradually replaced by BO_3 units as the PbO concentration increases (15–20 mol.-%) and PbO_4 pyramids form in place of Pb^{2+} ions. The modifications of the BO_3 units referred to above start to occur above 30 mol.-% PbO.[81] Other detailed studies of PbO–B_2O_3 glass structures have been carried out.[4, 59, 82,]

The viscosity which increases with the addition of boric oxide, has been studied[84, 85] and the refractive indices and specific gravities[83] of PbO–B_2O_3 glasses are reported.

The formation of a lead borate at the interface of litharge and a borosilicate glass, and its immediate subsequent dissolution in the glass, have been postulated to explain the definite interaction observed between the two.[6] Surface tension of lead borate melts has received certain attention in relation to 'crawling' of ceramic glazes. Changes may be briefly summarized for PbO contents of 75–92% by the following:

$$\left.\begin{array}{ll} 75\text{–}82{\cdot}5\% & d\gamma/dT \text{ negative} \\ 82{\cdot}5\text{–}84\% & d\gamma/dT \to 0 \\ 88\text{–}92\% & d\gamma/dT \text{ positive} \end{array}\right\} \begin{array}{l} \text{At temperatures between} \\ 600^\circ \text{ and } 1100^\circ\text{C} \\ \text{(ref. 86)} \end{array}$$

These surface tension anomalies of PbO–B_2O_3 melts have been reviewed.[87] The heats of solution in 2N nitric acid of several glasses[88] and devitrified borates[89] in the PbO–B_2O_3 system have been determined.

Lead borates dissolve in polyhydric alcohols (e.g. ethylene glycol) to the extent of 55% or less to provide a borate solution stated to be suitable for coating metals, etc.[90] When PbO or Pb_3O_4 dissolves in molten borax to form a borax bead, thermochromatic reversibility is shown.[91]

Many ternary and more complex systems have been studied and are summarized below.

Li_2O–PbO–B_2O_3	Fusibility diagrams plotted (950–1400°C). Densities studied, max. *d.d* = 4·3. Refractive indices, chemical stability, thermal expansions and water resistance of glasses. (Ref. 92)
Na_2O–PbO–B_2O_3	Thermodynamic properties of PbO dissolved in molten borax, studied by e.m.f. of $M\|soln\|O_2$ all at 720–820°C. Compound $PbO,3Na_2O,6B_2O_3$ found. (Ref. 93)
PbO–BaO–TiO_2–B_2O_3	No borates identified as solid phases. (Ref. 39)
ZnO–PbO–B_2O_3	See section on zinc borates (p. 572). (Group II refs. 375, 439–43; see p. 590)
$CdWO_4$–PbO–B_2O_3	$4PbO,B_2O_3$ formed, but no ternary compound. (Ref. 94)
Al_2O_3–SiO_2–PbO–B_2O_3	Coeff. of expansion of glasses (solder). (Ref. 28)
AlF_3–PbO–B_2O_3	Vitreous, crystallizing and sintering regions determined. Suitable as optical glasses. (Ref. 38)
PbO–Al_2O_3–B_2O_3	Supercritical fluctuations. (Ref. 144)
SiO_2–PbO–B_2O_3	(a) 90% of system occupied by $PbO,2B_2O_3$ and SiO_2. Crystallization curves given together with field boundaries and eutectic points. Stable, low m.p. glasses with high refractive indices. (Ref. 95) (See Figs. 40, 41) (b) Coefficients of expansion studied for glasses. (Ref. 28)

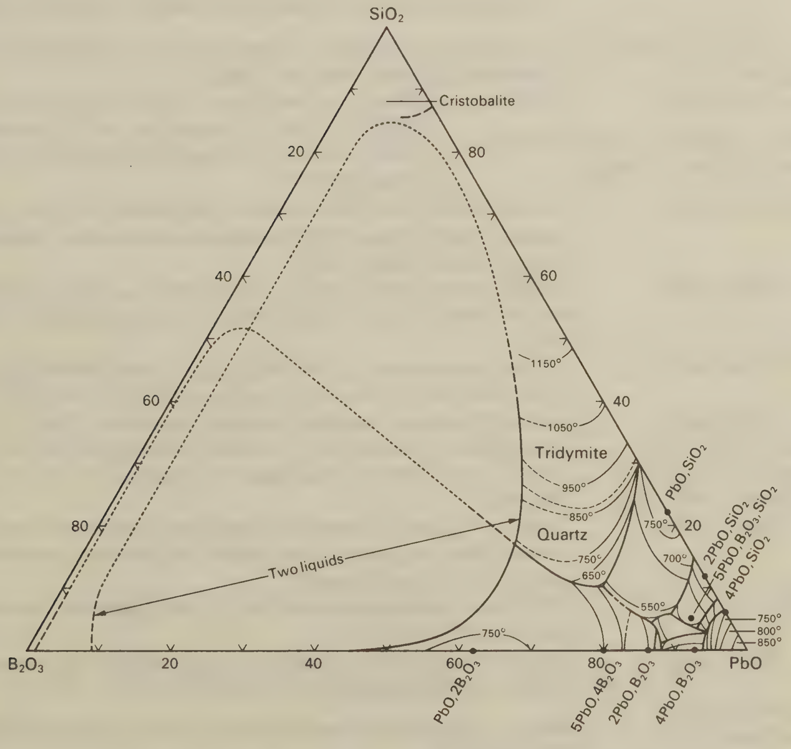


FIG. 41.—Phase diagram of system PbO–B_2O_3–SiO_2[95]

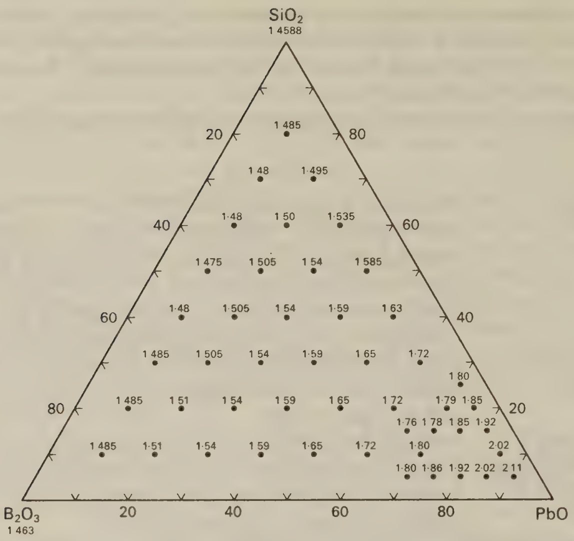


FIG. 42.—Average refractive indices of glasses in the system PbO–B$_2$O$_3$–SiO$_2$[95]

	(c) Investigated for decomposition reactions. (Ref. 76) (d) Detailed study of system; little change from previous work where >60% PbO. Immiscibility (2 liquid) areas determined. Also areas of metastable immiscibility studied for system containing >40% SiO$_2$. (Ref. 29)
SiO$_2$–TiO$_2$–PbO–B$_2$O$_3$ TiO$_2$–PbO–B$_2$O$_3$	Crystallization studies in these systems by application of differential thermal analysis. (Ref. 8)
TiO$_2$–PbO–B$_2$O$_3$	PbTiO$_3$ crystallizes very well from this system. (Ref. 96)
PbTiO + PbZrO$_3$–(50PbO + 50B$_2$O$_3$ PbZrO–(50PbO + 50B$_2$O$_3$)	PbO,B$_2$O$_3$,ZrO$_2$ formed as solid crystalline phase. See also zirconium borates (p. 618). (Refs. 40, 45)
PbO–WO$_3$–B$_2$O$_3$	15PbO,3B$_2$O$_3$,2WO$_3$ which melts congruently at 780°C, plus several binary phases. The system contains seven invariant ternary points. (Ref. 141)
PbO–MoO$_3$–B$_2$O$_3$	15PbO,3B$_2$O$_3$,2MoO$_3$ melts congruently at 772°C. System has six eutectics at 700, 620, 480, 510, 520 and 520°C. (Ref. 142)
PbO–V$_2$O$_5$–B$_2$O$_3$	Ternary compounds 12PbO,B$_2$O$_3$,V$_2$O$_5$ and 20PbO,3B$_2$O$_3$,-V$_2$O$_5$ exist in the subsolidus region at 550°C. (Ref. 143)
PbO–CrO$_3$–B$_2$O$_3$	The melts show a tendency to glass formation. (Ref. 159)
Nb$_2$O$_5$–PbO–B$_2$O$_3$ PbNb$_2$O$_6$–PbTiO$_3$–(50PbO + 50B$_2$O$_3$)	Crystallizing surface of systems investigated at up to 1100°C. No borate crystallization reported. (Ref. 41) (see Fig. 43)
PbO–Bi$_2$O$_3$–B$_2$O$_3$	Zones of glass formation determined and structure discussed. Very high refractive indices and dielectric constants. (Refs. 38, 97) (see Fig. 44)
Pb–Bi–B$_2$O$_3$	With increasing amounts of B$_2$O$_3$ metallic phase becomes richer in Pb. (Ref. 98)
PbF$_2$–PbO–B$_2$O$_3$	Use of this system discussed as a medium for growing yttrium aluminium garnets. (Ref. 90)
PbO–Fe$_2$O$_3$–B$_2$O$_3$ PbO–CuO–B$_2$O$_3$ PbO–TiO$_2$–B$_2$O$_3$	Electric conductance and structure of the molten systems. (Refs. 145–7)

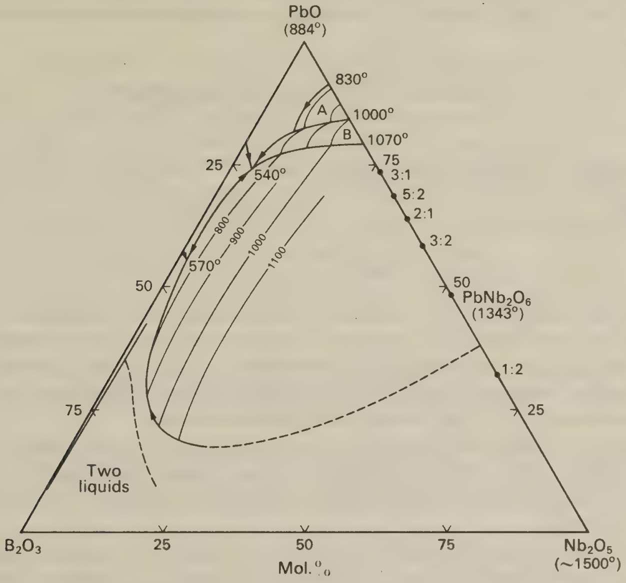


FIG. 43.—Phase diagram for the system $PbO–B_2O_3–Nb_2O_5$[41]

Binary lead niobate phases A and B are unstable and decompose in the ternary system at 588 and 730°C, respectively

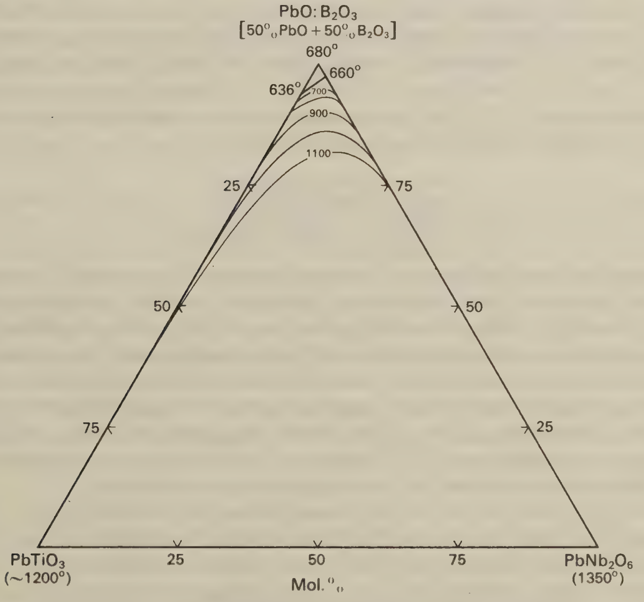
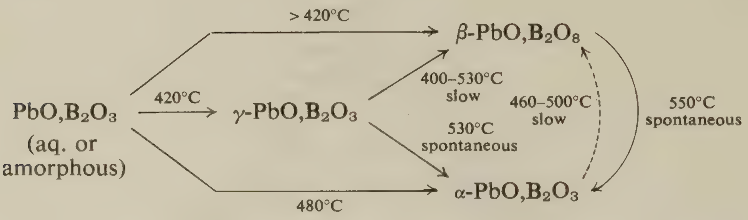


FIG. 44.—The system $PbO:B_2O_3–PbTiO_3–PbNb_2O_6$; crystallization surface of solid solutions[41]

PbO,B_2O_3. It was not until 1967 that definite proof of the existence of this compound was given.[72] It was found to exist as three metastable monotropic modifications in the $PbO–B_2O_3$ system. The interconversion of the three monotropes is shown below.



X-Ray powder diagrams of α-, β-, and γ-metaborates are recorded.[72] An earlier investigation of the $PbO–B_2O_3$ system[71] showed an area of metastability which was not at that time investigated. The existence of the 1:1 lead borate was postulated in an earlier investigation of the $PbO–B_2O_3$ system which was later criticized for the non-attainment of proper equilibrium conditions.[70]

The theoretical energy of formation was determined by an investigation of the $Pb|PbO,B_2O_3|Pt|O_2$ gas cell.[100] PbO,B_2O_3 melts have been used to grow good crystals of $PbTiO_3$[101] and are an excellent solvent for $BaTiO_3$[102], with which compounds are formed.

The surface tension of a 1:1 melt is reported to be 100 dynes/cm. Optical absorption data have been obtained for the PbO,B_2O_3 glass.[103] Further properties of the glasses with PbO,B_2O_3 composition are referred to elsewhere (see above).

$PbO,2B_2O_3$. This compound is the most easily formed compound of the system $PbO–B_2O_3$; it was isolated and identified in all the investigations of the system[70, 71, 97] and is the solid phase most likely to be crystallized from it at 2–83% PbO. With silica it is the solid phase which predominates over 90% of the $PbO–SiO_2–B_2O_3$ system[95]; it is also found as a solid phase in the $PbO–ZnO–B_2O_3$ system.[104]

The compound has been given a melting point of 768°C[71] but another investigator mentions a slightly higher figure of 780°C.[105] Various thermodynamic properties have been obtained.[100, 106] The thermodynamic data relating to the transition of crystalline $PbO,2B_2O_3$ to the glassy state at 25°C [106]

$$\begin{aligned}\Delta G &= 16{\cdot}7 \text{ kcal/mole}\\ \Delta H &= 22{\cdot}8 \text{ kcal/mole}\\ \Delta S &= 20{\cdot}2 \text{ cal/°C/mole}\end{aligned}$$

suggests large structural differences between the glassy and crystalline states.

The crystal growth of lead tetraborate from its melt has received detailed attention.[136–40] The effect of melt composition on growth rate can be explained in terms of the structural units present in the melt and their mobility near the crystal–melt interface.[138–9] Water affects the growth rate.[136] When trace amounts of CoO and SiO_2 were added to stoichiometric melts, each impurity in concentrations of 500 p.p.m. decreased the growth rate in the $\bar{c}$ direction by approximately 40%, while growth in the $\bar{a}$ direction was unchanged.[135] The effect of dissolved tungsten carbide on growth spirals and hillocks was studied by scanning electron microscopy.[140]

$PbO,2B_2O_3$ has been found to be isomorphous with $SrO,2B_2O_3$ (*q.v.*)[107], and although only the latter compound has been studied thoroughly it may be assumed that in the lead borate as well all the boron atoms are tetrahedrally co-ordinated and have the unusual characteristic that some oxygen atoms are common to three tetrahedra.[108] It is classified in the order of three-dimensional lattice borates containing double-ring structures.[109] X-Ray powder diagrams have been recorded.[71, 72, 80]

$PbO,3B_2O_3$. This compound is mentioned as being a solid phase in a study of the $PbO–B_2O_3$ system[70] and stated earlier (Mellor, V, p. 106) to be formed on fusing lead carbonate and boric acid and leaching with water to remove unreacted boric oxide. It has not, however, been reported more recently, and no characterization by physical methods is recorded.

$2PbO,B_2O_3$. $2PbO,B_2O_3$ exists in two polymorphic forms, the α-form being the primary phase in compositions containing from 87·3 to 88·0% of PbO, while the β-form does not appear at the liquidus.[71] Both forms are also found in a study of the $PbO–ZnO–B_2O_3$ system.[104] α-$2PbO,B_2O_3$ melts incongruently at 497°C to give $5PbO,4B_2O_3$ and a liquid. β-$2PbO,B_2O_3$ apparently inverts irreversibly to the α-form at about 473°C.[71] From X-ray data[71, 80] the structure has been placed in the category of 'non-ring borates with dimers of $B(O,OH)_3$ triangles and $B(O,OH)_4$ tetrahedra'.[109]

In the system $PbO–Pb(BO_2)_2–CdWO_4$, the latter component does not form a complex with the borates, but mixtures of $2PbO,B_2O_3$ and $CdWO_4$ crystallize together.[94]

$2PbO,5B_2O_3$. The only reference to this compound is in the original study of the $PbO–B_2O_3$ system[70] on which some doubt has since been cast.[71]

$3PbO,B_2O_3$. By normal nomenclature this compound may be called the orthoborate but no method of formation has been described. By thermodynamic calculations, however, the heat of formation for the orthoborate has been estimated to be −2·75 kcal/mole.[100] A 3:1 borate is mentioned as an ingredient in a magnetic composition also containing ferric, nickel and zinc oxides, but this may be a glass analyzing to the above formula.[110]

$4PbO,B_2O_3$. $4PbO,B_2O_3$ is the primary phase (in the β-form) crystallizing from a $PbO–B_2O_3$ melt containing 88 to 91·7% of PbO and (in the α-form) from 91·7 to 100% PbO.[71] The actual melting temperature of β-$4PbO,B_2O_3$ is confused by its transformation at about 552°C (maximum rate) and can only be estimated to be 555°C. α-$4PbO,B_2O_3$ melts congruently at 565°C and probably does not revert to the β-form.[71] These phases are also mentioned in some work on the $PbO–ZnO–B_2O_3$ system[104] and also forms mixed solid phases with $CdWO_4$ in the $PbO–Pb(BO_2)_2–CdWO_4$ system, as does $2PbO,B_2O_3$ (*q.v.*).

An n.m.r. study of crystalline lead borates and the corresponding glasses indicates little difference in structure, except in the case of β-$4PbO,B_2O_3$.

$5PbO,4B_2O_3$ and $9PbO,8B_2O_3$. Both these compounds have been identified in the metastable portion of the $PbO–B_2O_3$ system studied in detail in 1967.[65] It appears that the 5:4 borate can be in metastable equilibrium with the 1:2 borate in one part of the system and with α-PbO,B_2O_3 in another; and both 5:4 and 9:8 borates can be in metastable equilibrium together, in another. The 9:8 borate is also found in equilibrium with α-PbO,B_2O_3. The 5:4 borate was identified as a diffuse phase in the earlier study of the system[71] and it is of interest that the samples of $5PbO,4B_2O_3$ used in this study were later studied by X-ray techniques and reported to be more likely $9PbO,8B_2O_3$.[80] This was probably due to a slow reversion. Indexed X-ray powder diagrams are available for both compounds.[72] The 5:4 compound is reported as melting incongruently at 548°C and the crystals as being doubly refracting.[71]

$6PbO,5B_2O_3$. This compound is triclinic, with *d* (calc.) = 6·183.[130]

Anhydrous Lead Borates Containing Other Elements

Sodium. PbO reacts with molten borax to give the compound $3Na_2O,PbO,6B_2O_3$.[93]

Zinc. Three ternary phases were identified in tempered melts of the $PbO–ZnO–B_2O_3$ system: $PbO,2ZnO,B_2O_3$; $2PbO,ZnO,B_2O_3$; $4PbO,2ZnO,5B_2O_3$.[104, 111]

Silicon. There are probably many lead borosilicates. However, only two have been specifically identified: $PbO,3B_2O_3,SiO_2$ (which is converted into lead sulphate in the presence of sulphur dioxide at 550°C, to the extent of 15%[112]) and $5PbO,B_2O_3,SiO_2$ (which has an apatite structure[113]). X-Ray powder data and linear thermal expansion data for lead borosilicates in general are available.[114]

Zirconium. PbO,ZrO_2,B_2O_3 crystallizes from the system $(50PbO+50B_2O_3)$–$PbZrO_3$ at 600°C[45] and from the more complex system $(50PbO+50B_2O_3)$–$PbTiO_3$–$PbZrO_3$ at 1000°C.[40]

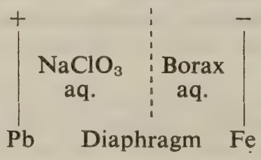
Vanadium. If lead monoxide, carbonate or hydroxide is fused with vanadium pentoxide and excess boric oxide at 1000°C for several hours in stoichiometric ratio ($Pb:V=1:1$) $2PbO,V_2O_5,B_2O_3$ is obtained. If the ratio $Pb:V=1:2$, a compound PbO,V_2O_5,B_2O_3 with a 10% excess of V_2O_5 is produced.[115]

Hydrated Lead Borates

A variety of basic lead borates of variable composition are precipitated from borate solutions at high pH. The composition of the precipitates is related to the temperature, the concentrations of the constituents and the washing of the precipitate. A review of all earlier attempts to produce lead borates of definite composition stated that there was no evidence for the formation of a simple lead borate. All previous workers had produced basic lead borates and these were often contaminated with the precipitating agent, lead nitrate; washing to remove it only caused hydrolysis.[116] Somewhat later it was suggested that there were only two identifiable basic borates of lead produced by precipitation from borax solutions[117,118]:

(a) Lead nitrate added to 0·1M borax → PbO,B_2O_3,xH_2O.
(b) Lead nitrate added to 0·1M borax in 0.075–0·125M sodium hydroxide → $7PbO,2B_2O_3,xH_2O$.

An indeterminate compound which is probably a basic borate is formed by passing a current through the following cell[119]:



Slightly previous to the main work on the subject of the formation of characterized lead borates the following statements were made, based on experimental observations:

(1) No evidence could be found for the formation of hydrated lead borates with $B_2O_3:PbO$ ratio greater than one.
(2) Lead borates precipitated from alkali borates adsorbed the latter.
(3) The product formed from lead acetate and boric acid was not altered by the addition of ammonia, but if the lead acetate/ammonia ratio was kept constant, the precipitate approached a 1:1 lead borate if the boric acid was in very large excess.[120]

Russian workers have extended the work on the production of lead borates from lead acetate and boric acid. They state that crystalline borates can be produced only at low pH values, i.e. using boric acid as the borate source.[105] The system PbO–B_2O_3–H_2O at 75°C has recently been studied[53,148–50] and the solubility of the solid phases $4PbO,5B_2O_3,2{\cdot}5H_2O$, $PbO,2B_2O_3,3H_2O$ and $3PbO,10B_2O_3,9H_2O$ determined.

The best-characterized lead borate with well-developed crystalline form is $PbO,2B_2O_3,4H_2O$. If a mixture of boric acid and lead acetate solution is vigorously stirred, with heating, for several days, grains of this borate crystallize at first as the acetic acid evaporates. Later the crystalline habit changes and long needles form. Alternatively, a mixture of lead acetate and boric acid in a 1:2 molar ratio may be ground together, moistened and left to evaporate, when fan-like aggregated crystals form. For larger quantities it is possible to start with a suspension of crystals prepared as described above and then to add small quantities of litharge and boric acid in the stoichiometric ratio; so long as there is plenty of 'seed' present the crystals will grow from these reactants.[105]

The compound hydrolyses slightly in water and forms an opalescent solution (colloidal?) containing about 0·7 g/l, which on heating with hydrogen sulphide gives colloidal lead sulphide. Lead sulphide is also formed by reaction of a suspension of the borate with ammonium hydrosulphide or sodium sulphide solution, ammonium or sodium borates being the soluble products.[121] The compound dehydrates by losing the first water of crystallization between 50 and 95°C, forming a very hygroscopic compound. On heating between 130 and 170°C two more molecules of water are lost, and all the water is finally expelled at a temperature somewhat over 300°C. $PbO,2B_2O_3,4H_2O$ has a density of 3·05 at 25°C.[105]

Another lead borate, $4PbO,5B_2O_3,2\frac{1}{2}H_2O$, is formed directly from the action of boric acid on litharge. Its solubility, heat capacity and some other thermophysical properties have been determined.[122]

Using as a starting point the 1:2:4 borate, two other lead borate hydrates have been formed:

(a) The 1:2:4 borate is dissolved in hot lead acetate solution. As it cools $PbO,2H_2O$ crystallizes and the pH of the solution decreases; when the 'hydroxide' has precipitated, large crystals of indefinite form crystallize analyzing at $2PbO,B_2O_3,5H_2O$, but a pure borate of this composition has yet to be formed.[105]

(b) A metaborate has been prepared by dissolving $PbO,2B_2O_3,4H_2O$ in hot 10% lead acetate solution to which acetic acid has been added, and cooling. The compound $PbO,B_2O_3,2H_2O$ is formed. It loses 1 molecule of water on being removed from the reaction media. As yet, neither hydrate has been obtained in a pure state.[105]

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BORATES OF GROUP VI

Boron oxy-compounds of chromium, molybdenum, tungsten and uranium are considered separately (Section A13).

BORATES OF GROUP VII

MANGANESE BORATES

Anhydrous Manganese Borates

There has been little published work on the production of simple anhydrous manganese borates since the work done by earlier workers and described in Mellor, V, 113. Good evidence then existed for the 1:2 and 3:1 crystalline compounds. Borates with ratios 3:2, 2:1 and 1:1 were not so well substantiated. With the exception of the 3:2 borate all have been quoted in more recent publications.

Paramagnetic resonance absorption of microwaves is shown by MnO,B_2O_3 at room temperature.[1] $MnO,2B_2O_3$ behaves in much the same way.[2, 31] The energies of formation of both MnO,B_2O_3 and the orthorhombic $2MnO,B_2O_3$ were calculated from the e.m.f.'s of the cell.

$$Mn(liq.)|MnO,B_2O_3|Pt|O_2(gas)$$

and found to be −4·48 kcal/mole and −5·73 kcal/mole, respectively.[4] The 1:2 borate is only slightly reduced by hydrogen at temperatures up to 600°C. It has the capacity to absorb either by chemisorption or into the lattice appreciable quantities of hydrogen, quantities which increase as the temperature rises.[5]

A triclinic modification of $2MnO,B_2O_3$ has been reported and is said to be isostructural with the 2:1 iron and cobalt borates.[6] This compound has been used as a catalyst for the production of polycarbonate resins[7–9] and as damper to the luminescence of $2CdO,B_2O_3$ if used in quantities greater than 1 mol.-%.[10]

The orthoborate ($3MnO,B_2O_3$) has been studied[11, 29] to determine its infra-red spectrum, which suggests a dimeric arrangement of the $(BO_3)^{3-}$ ions; it is not known whether they are planar or pyramidal.[11] Antiferromagnetism of the orthoborate has

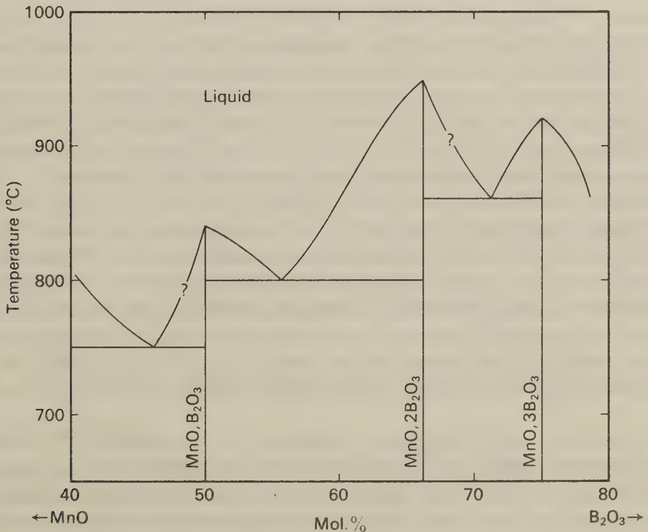

FIG. 45.—Phase diagram for the system $MnO–B_2O_3$[12]

been studied in conjunction with the 3:1 nickel and cobalt borates.[31] It is also found as the mineral *jimboite*.

The system $MnO–B_2O_3$ has been studied together with other metal borate systems, but some doubt has been cast on the time allowed for equilibrium to be attained in these systems (cf. lead borates). The solid phases reported were MnO,B_2O_3, $MnO,2B_2O_3$, and $MnO,3B_2O_3$[12] (see Fig. 45). Manganese diborate, MnB_4O_7, has an orthorhombic crystal structure with $d = 2{\cdot}87$.[31] Lattice parameters are given and magnetic properties described.

Anhydrous Manganese Borates Containing Other Elements

$Li_2O,2MnO,B_2O_3$ is the only alkali-metal manganese borate synthesized as yet; it is formed by heating manganese oxide with an excess of Li_2O,B_2O_3. The reaction has been studied by differential thermal analysis and a crystal structure study carried out[13] on the product.

Strictly not a borate, but mentioned here because it contains manganese, boron and oxygen is $Mn(B_2O(OCO,CH_3)_5)_2$ which is formed from diboron oxide tetraacetate and manganese acetate. The infra-red spectrum of this compound has been studied and magnetic measurements made, showing that it belongs to the octahedral high-spin type of complex.[14]

MnO,SnO_2,B_2O_3 is synthesized in the same manner as many other bivalent metal tin borates by heating a manganese salt with tin dioxide and boric acid or borax in an autoclave.[15] Its crystal structure (which is of dolomite type[18]) and stability have been studied.[16, 17, 30]

Manganese bromo- and iodo-boracites, $5MnO,7B_2O_3,MnBr_2$ and $5MnO,7B_2O_3,MnI_2$ have been synthesized from melts of the appropriate oxides and halides, and their crystalline structure compared with the chloroboracites.[19] The mineral *chambersite* is a chloroboracite containing manganese. It, and the other two mentioned here, may also be prepared by the method described earlier under magnesium boracites.[20]

The only anhydrous manganese borates not previously mentioned are the minerals, *pinakiolite* which is a substituted ludwigite and can be represented by the formula $4(Mg,Mn^{II})Mn_2O_3,B_2O_3$ (cf. *boroferrite*), and *kurchatovite*, $6CaO,5MgO,MnO,6B_2O_3$.

Hydrated Manganese Borates

The addition of manganese salts to borate solutions causes the precipitation of a variety of hydrated, non-crystalline manganese borates, the composition of which depends on the ratio of the reacting substances. Under the correct conditions two crystalline manganese borate hydrates, $MnO,2B_2O_3,9H_2O$ and $MnO,3B_2O_3,8H_2O$ have been formed. However, some of the apparently amorphous precipitates seem to have consistent composition and might be classified as true compounds. Their precipitation occurs at the same pH as precipitation of the hydroxide.[21] $MnO,3B_2O_3,7{\cdot}5H_2O$ has been described, but may be a solid solution (see below). The insolubility of the precipitates suggested a method of removing borate impurities found in Chile saltpetre; the precipitates could be used in paints and cosmetics.[22] Manganese borates have been used as driers in paints and also in blowing linseed oil, for which a relatively impure borate is adequate; this may be made by treating iron-containing pyrolusite with sulphuric acid and adding borax to the extract to obtain the manganese borate.[23]

A detailed study of the formation of these variable compounds by metathetic reactions between borax solutions and manganese salts has been carried out.[24]

MnO,B_2O_3,xH_2O. Older references describe the formation of hydrated metaborates by the slow addition of manganese sulphate solutions to borax solutions; their solubility and effectiveness as paint driers is also mentioned (Mellor, V, 112). Later work describes the formation of a metaborate of indeterminate hydration and having a $MnO:B_2O_3$ ratio of 1·03. It was found that a ratio as near to the metaborate ratio as this could be obtained by adding a solution containing 2 moles of manganese sulphate to a solution of 1 mole of borax and 2 moles of potassium hydroxide. Alkali/B_2O_3 ratios different from this produced manganese borates other than metaborates.[25] The 1:1:3 compound was made from $MnCl_2$ and $Na_2B_4O_7$ in aqueous alkali halide media.[39] A patent describing this latter technique has been filed, although using caustic soda rather than caustic potash.[26] The thermal decomposition of the 1:1:3 amorphous hydrate has been studied.[37]

$MnO,2B_2O_3,9H_2O$. This is a well-defined crystalline borate, formed by a two-stage process. The first reaction is to produce a manganese borate approximately corresponding to $2MnO,3B_2O_3,xH_2O$ by mixing equimolar (0·1M) solutions of borax and manganous chloride. After filtration, the precipitate is suspended in a 0·2M boric acid solution, containing sufficient of the acid to convert it into $MnO,2B_2O_3,xH_2O$, together with about 60% in excess to avoid hydrolysis of the product. Crystallization starting otherwise in 1–3 days, can be accelerated by seeding or agitation. By adding more reactants to the slurry and maintaining the pH at 7·5, further quantities of crystals can be obtained. Alternatively, the crystals are formed by hydrolysis of the hexaborate, $MnO,3B_2O_3,8H_2O$.[25]

The crystal structure has been determined and shown to be triclinic, with *d* (expl.) = 1·8.[32, 33] The structure is composed of isolated polyanions of $[B_4O_5(OH)_4]^{2-}$ bound by Mn^{2+} cations and intermolecular hydrogen bonds, the polyanions themselves consisting of BO_4 tetrahedra and BO_3 triangles joined by apices to form 6-membered rings. The product is stable up to 50°C, but 6 molecules of water are lost between 50 and 70°C, producing a highly hygroscopic material. At 70–100°C a further molecule of water is removed and the compound loses its hygroscopicity. The last 2 molecules of water of crystallization are not lost until 350°C is reached. Hydrolysis is slow, equilibrium being reached after about a month. The presence of boric acid retards hydrolysis, but as the boric acid content increases the solubility increases. The crystals are stable in solutions with a pH range of 6·8–8·5.[25]

$MnO,3B_2O_3,7{\cdot}5H_2O$. Russian workers have studied this composition in detail.[34–6] Thermal decomposition entails the formation of two intermediate pentahydrates, one crystalline and the other amorphous, and a crystalline anhydrous 1:3 product.[34] Dehydration proceeds as a 0·5th order reaction with activation energy of 13–16 kcal/mole. In their latest work they regard the material to be a solid solution on the basis of D.T.A. curves and isomorphism with related iron and cobalt compositions.[36]

$MnO,3B_2O_3,8H_2O$. This borate is also formed in a two-stage process (cf. 1:2:9 borate, above) by suspending the amorphous 2:3:*x* borate in warm 10% boric acid and vigorously agitating; the precipitate dissolves after an hour or two. The solution is then left to crystallize over a period of a day or two. Thin transparent platelets form which have a density of 1·94 at 25°C and have similar characteristics with respect to thermal dehydration, hydrolysis and solubility as $MnO,2B_2O_3,9H_2O$.[25] An alternative method, which produces a somewhat impure product, is to mix warm solutions of borax (~15%) with four times the molar concentration of boric acid and 1 molar proportion of manganous chloride, with rapid agitation; the mixture clarifies and, on standing, crystallizes.[25]

Infra-red absorption spectra of the hydrated hexaborates have been determined.[38]

Hydrated Manganese Borates Containing Other Elements

Potassium and Ammonium

If the amorphous 2:3:*x* borate, or the crystalline 1:3:8 borate mentioned above, is dissolved in a potassium polyborate solution ($K_2O,2B_2O_3 + H_3BO_3$) and then allowed to crystallize, the compound $K_2O,MnO,6B_2O_3,11H_2O$ is formed.[25] This borate loses its water of crystallization in the following manner: 4 molecules are lost at 105°C, a further 3 at 150°C, 2 more at 200°C and the last 2 by gradually heating to 300–450°C. It has a density of 2·01 and hydrolyses in water.[25]

By substituting ammonium borate for potassium borate, the analogous ammonium compound is formed, i.e. $(NH_4)_2O,MnO,6B_2O_3,11H_2O$.[25]

Borotartrates and Borotrihydroxyglutarates

These compounds are formed by treating a manganese borate with a solution of an alkali tartrate or trihydroxyglutarate.[27] The decomposition of manganese borotartrates on hydrolysis has been studied.[28]

Hydrated Borate Minerals Containing Manganese

Sussexite	$2(Mn,Mg)O,B_2O_3,H_2O$
Powerite	$(Mn,Mg,Zn)O,CaO,B_2O_3,H_2O$
Axinite	$2(Fe,Mn)O,2Al_2O_3,4CaO,B_2O_3,8SiO_2,H_2O$
Tourmaline	$(Na,Ca)R_3(Al,Fe)_6B_3Si_6O_{27}(O,OH,F)_4$ where $R = Mn^{II}$, Mg, Fe^{II}, Fe^{III}, Al, Li, Cr
Seamanite	$3MnO,B_2O_3,Mn_3(PO_4)_2,6H_2O$.

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BORATES OF GROUP VIII

IRON BORATES

Anhydrous Iron Borates

Earlier work on iron borates (Mellor, V, 114) mentions only one synthetic anhydrous borate having the formula $2FeO,Fe_2O_3,3B_2O_3$ and crystallizing from the lower layer of a fused mixture of ferrous oxide and boric acid. No further reference to this compound has since been made, although other ferrous, ferric and ferrosoferric borates have been synthesized. Six borates of these types are known as well as mixed borates containing tin and vanadium; a ferrous boracite is also known. In addition to these well-defined borates an early reference indicates that the ferrous 2:1, 5:1 and 6:1 borates are formed by fusing various proportions of ferrous oxalate with boric oxide at 1000–1400°C.[9] Fresh evidence for the formation of these borates as true compounds has not been forthcoming; it is possible that they were glasses, although the authors of this work quoted crystallographic data and supplied photomicrographs of the crystals.[1] More recently still, a study of the Fe_2O_3–B_2O_3 system at 670–900°C has indicated Fe_2O_3,B_2O_3 to be the stable phase up to 800°C, when the $Fe_2O_3:B_2O_3$ ratio is between 0·25 and 2·6. At 750°C when the ratio is between 1·0 and 2·6 two phases exist, Fe_2O_3,B_2O_3 and $3Fe_2O_3,B_2O_3$. Above a ratio of 2·6, only $3Fe_2O_3,B_2O_3$ and α-Fe_2O_3 exist.[3] $FeBO_3$ decomposes at 900–920°C to give Fe_2O_3 and amorphous B_2O_3; if the reaction mixture is allowed to stand at 910–975° for 2 days, Fe_3BO_6 is formed but no stable borate exists above 975°C.[127] Phase relationship within the Fe_2O_3–B_2O_3 system, with special relationship to single crystal growth of $FeBO_3$ (see below) has also been described.[130]

The system BaO–Fe_2O_3–B_2O_3 has been studied to examine the possibility of obtaining crystalline magnetic materials. Such were found[2] but did not contain the borate radical.[4] Another system studied to determine the boundaries of crystal formation was Li_2O–Fe_2O_3–B_2O_3.[5] Glasses formed from molten borax and having iron contents from 3·3–8·11% were shown to be paramagnetic.[6] Electrolysis of ferric oxide dissolved in borax at elevated temperatures was characterized by chemical polarization.[7] Well-developed polarographic waves were obtained at 820°C.[8]

Ferrous Borates

FeO,B_2O_3. Although this compound is reported, together with $4FeO,Fe_2O_3,B_2O_3$, to be present in the scales formed during the surface oxidation of iron-boron alloys containing 0·04–4·2 wt.-% of boron at 800–1000°C, the evidence may not be conclusive.[9]

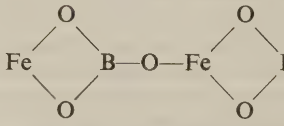
$FeO,2B_2O_3$. This compound is formed under hydrothermal reaction conditions when ferrous oxalate and boric acid react together and the B_2O_3 concentration is allowed to fall to within the range 45–50%. It is stable over the temperature range 250–700°C. It occurs as short columnar or prismatic crystals with a pink or yellow-orange coloration, when formed at lower temperatures; formation at 700°C gives colourless crystals. It has a density of 2·94.[10]

$2FeO,B_2O_3$. Both cobalt and nickel form a 2:1 borate, but there is no firm evidence that ferrous iron does. However, it may be significant that triclinic $2MgO,B_2O_3$ is quoted as being isostructural with manganese, iron and cobalt 2:1 borates.[11] It is as a consequence placed in the structural group of non-ring borates with dimers of $B(O,OH)_3$ triangles and $B(O,OH)_4$ tetrahedra ($Fe_2B_2O_5$).[12]

Refs. p. 647

Ferroso-Ferric Borates

$4FeO,Fe_2O_3,B_2O_3$. This compound is the most easily formed of all the iron borates and corresponds to the mineral *vonsenite* in the ludwigite family of minerals. The preparation of $4FeO,Fe_2O_3,B_2O_3$ has been carried out in various ways. Initially it was found by electrolysing sodium metaborate melts in a carbon crucible (which acted as a cathode) with an iron rod as an anode, at 950°C, for 1–2 hours at 25 A and less than 7 V. On leaching the electrolyte with hot dilute nitric acid, crystals of Fe_3O_4 and $4FeO,Fe_2O_3,B_2O_3$ were left.[13] The latter were shiny, black needles. They were also formed by heating a 2:3 ratio (by weight) of ferric oxide and anhydrous borax together in an inert atmosphere at 1000°C and then extracting with 3N nitric acid.[14] It is formed also under hydrothermal conditions of reaction, in the form of fine black acicular crystals, by heating ferrous oxalate and boric acid together under pressure. The field of existence under these conditions broadens as the temperature increases, e.g. at 250°C the borate is a stable phase at 0·5–2·2% B_2O_3; at 700°C the range is 2·3–45% B_2O_3.[10] Further work has been carried out showing that minerals of the *ludwigite-vonsenite* series result by reducing slightly alkaline or neutral solutions.[15] Oxidation of iron–boron alloys at 800–1000°C results in the formation of a scale which protects the alloy from further oxidation and is said to consist of FeO,B_2O_3 or $4FeO,Fe_2O_3,B_2O_3$.[16] The formation of $MgFe^{II}Fe^{III}BO_5$ and $Mg_2Fe^{III}BO_5$, members of the ludwigite series, is described.[17] $4FeO,Fe_2O_3,B_2O_3$ is attacked by dilute hydrochloric acid but less by sulphuric and nitric acids.[14] The structure has been shown to contain BO_3 triangles, rather than BO_4 tetrahedra[18], and a grouping such as:


(Ref. 14).

It is considered, in the system of borate structures, to be a 'tribasic monoborate with additional anions, in the order of insular borates'[12], a conclusion based on structural evidence of another worker.[19] A Mössbauer study of isomorphism in the ludwigite and vonsenite series has been made.[92]

An analogous compound with the ferric iron replaced by tervalent vanadium has been prepared by electrolysis of a molten borate mixture containing vanadium, ferrous and boric oxides, at 850–900°C. Crystallographic parameters are given for this compound, $4FeO,V_2O_3,B_2O_3$.[20]

Ferric Borates

Fe_2O_3,B_2O_3. The system Fe_2O_3–B_2O_3–H_2O was studied recently under hydrothermal conditions in an autoclave at 250–600°C. Three ferric borates were formed, one of them being Fe_2O_3,B_2O_3, another an indeterminate hydrate of it, and the third $3Fe_2O_3,B_2O_3$.[21] Compounds very close to ferric 1:1 borate have been produced from ferric oxide in a flux with the composition $Me_2O_3:Bi_2O_3:B_2O_3 = 1:1:5$ (where Me = Ga, Cr or Ti) at 1200°C; the product was annealed at 900°C. A range of products of the general formula $Fe_{(2-x)}Me_xO_3B_2O_3$ was formed, e.g. $(Fe_{1\cdot8}Ga_{0\cdot2})O_3,B_2O_3$.[22] The X-ray diffraction powder diagrams of these compounds are virtually identical and have had their space-group assigned, showing that they have a calcite structure.[22] Absorption bands characteristic of independent BO_3 and BO_4 groups exist in the infra-red spectrum of the borate.[23, 89, 128–9]

Considerable attention has been given to the magnetic and magneto-optical properties of iron (III) borates, notably $FeBO_3$. The technique of growing single crystals for the purposes of these studies is highly developed[126, 130]; methods for obtaining the polycrystalline orthoborate with optical transparency in the visible part of the spectrum have also been described.[125, 152] Antiferromagnetic resonance has been measured at 4·2 K in the weakly ferromagnetic single crystal $FeBO_3$.[131–3] The weak magnetization was ascribed to a small canting of the antiferromagnetic sublattice[134], Mössbauer-effect measurements of the hyperfine interaction of the Fe nuclei were used in another study to examine the temperature dependence of sublattice magnetization.[142] Magneto-elastic properties have also been considered.[131, 135] Nuclear magnetic resonance (n.m.r.) studies have been made on the single crystals[136–9, 142] including reference to domain structure of $FeBO_3$.[139, 140] It was suggested that the domain walls are of the 120° Bloch type, lying a few degrees oblique to the basal plane.[140] Spin configurations of $FeBO_3$ above and below spin orientation temperatures were analysed by magnetic measurements and dopants found to induce a different spin configuration and orientation.[141] Faraday rotation at 77 K has been measured.[91] Raman scattering in $FeBO_3$ has been studied by several workers[90, 144–7], as have magneto-optical properties and the photomagnetic effect. The susceptibility of ferric borate may be changed by exposure to radiation of 0·4–1·1 μm at 77 K.[148–9] Variation in the intensity of coherent X-ray scattering on subjecting $FeBO_3$ crystals to a magnetic field has also been observed.[143]

Single crystals may be grown from melts containing borate ions and one or both of lead fluoride and lead oxide, such that $Pb:(Pb+B_2O_3)$ is between 23 and 33 mol.-% and $Fe_2O_3:(Fe_2O_3+B_2O_3)$ is between 17·5 and 30 mol.-%.

$3Fe_2O_3,B_2O_3$. Black crystalline platelets of this compound are found on leaching a sodium borate/ferric oxide reaction product. Equimolar quantities of $3Na_2O,$-B_2O_3 and ferric oxide are dried at 200°C, mixed, and heated at 1200°C for about 18 hours in a normal atmosphere. The crystals remaining after leaching the melt have been studied in an attempt to deduce the structural formula[24], which can be described empirically as $Fe_3[BO_4]O_2$ and placed in the same structural group as certain borates of Group V, e.g. $Ta(BO_4)$.[12] It has an orthorhombic habit.[24, 124] The borate is also formed under hydrothermal conditions. It is a solid phase in the system Fe_2O_3–B_2O_3–H_2O between 250° and 600°C[21] and may be formed by heating mixtures of γ-FeO(OH) and boric acid, with or without water, in an autoclave at 200–400°C.[26] The stability of $3Fe_2O_3,B_2O_3$ has been determined under various conditions.[23]

Anhydrous Iron Borates Containing Other Elements

A compound FeO,SnO_2,B_2O_3 has been prepared in an analogous manner to the calcium, magnesium, barium and manganese-stannic borates by hydrothermal reaction of ferrous oxide with stannic oxide and boric acid or borax.[27] The crystal structure of an iron-cobalt borate, $FeCoBO_4$, has been determined.[110] The corresponding warwickite-type $FeNiBO_4$ has been made by hydrothermal synthesis at very high pressure.[108] Crystallographic and magnetic properties of the boroferrites, $Fe_2O_3,$-$2MgO,B_2O_3$ and $Fe_2O_3,4NiO,B_2O_3$ have been studied.[109]

$5FeO,FeCl_2,7B_2O_3$, a ferrous boracite, may be formed in the usual way (see boracite) as well as the bromo- and iodo-analogues.[28, 29] The phase transitions of the iodo-compound at −40° to −120°C have been studied; it exists in monoclinic, rhombohedral and orthorhombic phases.[31] As with other boracites it has a three-dimensional lattice structure with no ring formation[12, 30] and is best written $Fe_3(B_7O_{13})Cl$. A ferrous derivative of diboron oxide tetra-acetate has been formed by reaction with ferrous acetate. The compound $Fe^{II}(B_2O(OCOCH_3)_5)_2$ has had its infra-red spectrum studied and various magnetic measurements made. Analogous magnesium, zinc, chromium, manganese, cobalt and nickel compounds are formed.[4]

The synthesis and structure of bismuth iron/aluminium borate has been discussed; its formula can be written $Bi_2O_3,3(Al/Fe)_2O_3,4B_2O_3$, where the Al:Fe ratio is 11:9.[81] The crystallization region of the system Y_2O_3–Fe_2O_3–$50PbO,$-$40PbF_2$–$10B_2O_3$ have been studied.[88]

Hydrated Iron Borates

Amorphous precipitates of ferrous and ferric borates of indeterminate composition are formed by the addition of ferrous or ferric salts to borax solutions (Mellor, V, 114). A large number of papers have been written on the formation and properties of 'iron borate' sols and jellies. Viscosity and pH changes have been studied during gel formation; explanations have been given for the rapid increase in viscosity and a 50% fall in the original hydrogen-ion concentration during the gelation period.[32] Changes in viscosity and electrical conductivity with temperature during gel formation have also been studied.[33, 34] 'Iron borate' gels show that the Liesegang phenomenon is observable during the coagulation of a ferric borate sol with potassium chloride or sulphate. The influence of concentration of coagulating electrolyte, time and temperature on syneresis of 'ferrous borate' jellies has been investigated.[36] It is significant that the empirical formulae of gelatinous precipitates formed when borax is added to ferric chloride solutions show Fe:B atomic ratios of 11:1 and 24:1[37], leading to a conclusion that the boron may only be adsorbed on ferric/ferrous hydroxide gels. This is supported by the effectiveness of ferric oxide gels in removing traces of borate from brines and the possibility of regeneration of the gels by rinsing with carbonated water.[38] The paramagnetic susceptibilities of colloidal 'ferric borate' produced by adding potassium borate to ferric chloride are higher than the separated solid 'ferric borates'.[39]

Hydrated Ferrous Borates

A well-characterized crystalline ferrous borate hydrate, $FeO,3B_2O_3,8H_2O$ was first formed in 1960 by adding a ferrous sulphate solution in de-aerated water to a sodium borate solution ($Na_2O:B_2O_3=1:4{\cdot}3$) and keeping the mixture in a carbon dioxide atmosphere for 3–4 days. The crystals had a density of 2·07, and their dehydration was studied.[40, 93] The same workers later synthesized $FeO,3B_2O_3,7{\cdot}5H_2O$ and determined its structure.[105] D.T.A. analysis showed it to be a solid solution. Activation energies for the dehydration were calculated.[106] Infra-red absorption spectra have been measured.[107] This compound is not found as a solid phase in the FeO–B_2O_3–H_2O system at temperatures between 250° and 700°C.[10]

Further compound formation was studied by investigating the reaction of ferrous oxalate with boric acid (or boric oxide) under hydrothermal conditions. As the oxalate decomposes at elevated temperatures (250–700°C), this amounted to a study of the FeO–B_2O_3–H_2O system.[10] Owing to the slowness of decomposition of the oxalate at lower temperatures in the above range, a synthesized borate was also used ($6FeO,7B_2O_3,H_2O$) as an alternative source of iron. $2FeO,B_2O_3,H_2O$ (analogous to ascharite, $2MgO,B_2O_3,H_2O$) is formed as white acicular and fine prismatic crystals. The field of existence narrows as the temperature increases. It occurs only in mixtures with vonsenite ($4FeO,Fe_2O_3,B_2O_3$) in the system at 450°C. It does not exist at 500°C. It has a density of 3·61 and its optical properties have been studied.[10]

$5FeO,10B_2O_3,4H_2O$ is stable at 250°C but does not occur in the system above 300°; at 250°C it is stable only in the range 25·5–50% B_2O_3. It exists as very small hexagonal platelets of golden coloration. Its density has not been determined.[10] $6FeO,7B_2O_3,H_2O$ is analogous to the boracite family with Cl_2 replaced by $2OH^-$. It is stable in the system over the range 250–650°C and at B_2O_3 concentrations in the range 20–45%. The crystals are cubic or octahedral and range in colour from light grey to yellow. The density is 3·52; optical data are recorded.[10]

In a more recent study of the FeO–B_2O_3–H_2O system at up to 250°C, three new borates were found: $FeB_4O_7,2{\cdot}5H_2O$; $FeB_6O_{10},4{\cdot}5H_2O$; and $FeB_{12}O_{19},5H_2O$.[101] The compounds FeB_4O_7, $Fe_6B_{14}O_{27},H_2O$, Fe_3BO_5, $FeB_4O_7,0{\cdot}8H_2O$ and $Fe_2B_2O_5,H_2O$ were all confirmed. A phase diagram was given.

Hydrated Ferric Borates

Ferric borates, $Fe_2O_3,3B_2O_3,3H_2O$ and $3Fe_2O_3,4B_2O_3,15H_2O$ have been isolated as crystalline solids.[41] A hydrothermal study of the Fe_2O_3–B_2O_3–H_2O system in the 250–600°C range between 30% and 70% B_2O_3 concentrations resulted in the formation only of the indeterminate hydrate Fe_2O_3,B_2O_3,nH_2O. This compound, where $n = 1$, 2, 3 or 4, has been prepared by the 'indifferent component method' from Fe_2O_3 and Na or K tetraborates in the presence of NaCl or KCl.[102, 103] The same workers had previously reacted $FeCl_3$ with borax to form $3Fe_2O_3,2B_2O_3,10H_2O$ which aged to the hexahydrate.[104] The other borates formed in this system were anhydrous (see above [21]).

Iron-Containing Borate Minerals

Warwickite	$3(Mg,Fe)O,TiO_2,B_2O_3$ (Mg > Fe).
Ludwigite	$4MgO,Fe_2O_3,B_2O_3$ and structurally similar minerals such as *paigeite* (*vonsenite*) and *hulsite*.
Lagonite	$2Fe_2O_3,3B_2O_3,3H_2O$ (may be a mixture).
Tourmaline	$(Na,Ca)R_3(Al,Fe)_6B_3Si_6O_{27}(O,OH,F)_4$ and associated minerals (R = Mg, Fe^{II}, Fe^{III}, Al, Li, Mn^{II} or Cr).
Axinite	$2(Fe,Mn)O,2Al_2O_3,4CaO,B_2O_3,8SiO_2,H_2O$ and associated minerals.
Sappihrine	$9MgO,10(Al,Fe,B)_2O_3,4SiO_2$.
Grandidierite	$2Na_2O,4FeO,8(Fe,Al,B)_2O_3,5SiO_2$.
Kornerupine	$(Mg,Fe^{II},Fe^{III},Al)_{40}(Si,B)_{18}O_{86}$.
Homilite	$3(Ca,Fe)O,B_2O_3,2SiO_2$.
Dumortierite	$(Al,Fe)_7O_3[BO_3][SiO_4]_3$.

COBALT BORATES

Anhydrous Cobalt Borates

Since the original edition of Mellor only one new simple cobalt borate has been synthesized, namely $4CoO,B_2O_3$.[42] A cobalt borate analogous to ludwigite has been formed containing both Co^{2+} and Co^{3+}, and may be written $4CoO,Co_2O_3,B_2O_3$.[43] A number of ternary borates containing cobalt have been synthesized.

The CoO–B_2O_3 system has been studied in detail. The only solid phases found

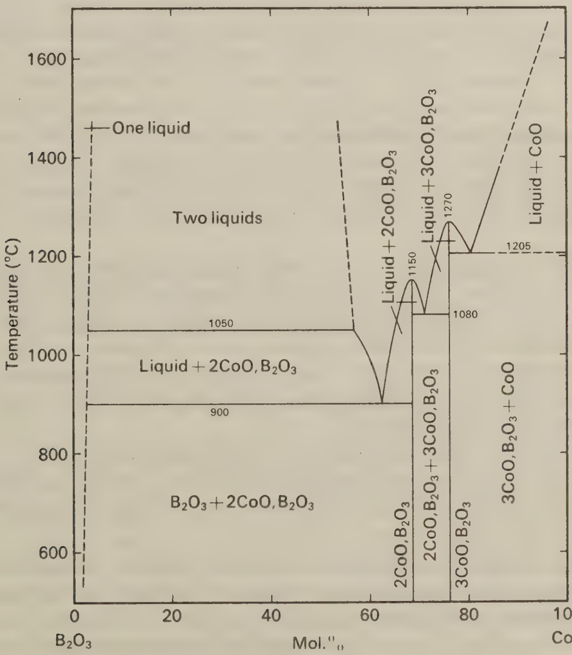


FIG. 46.—Phase diagram for the system CoO–B_2O_3.[44] Note that region designated as Liq + $2CoO,B_2O_3$ does not obey phase rule theory

Refs. p. 647

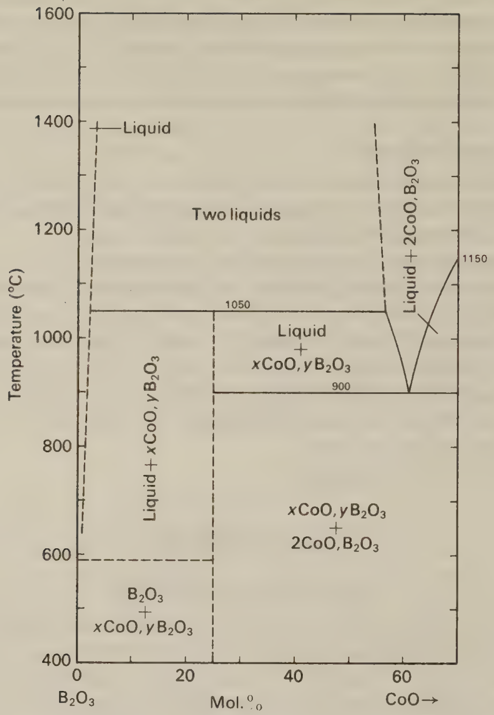


FIG. 47.—Revised form of phase diagram for the system CoO–B_2O_3[45]

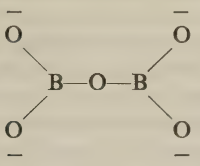
are $2CoO,B_2O_3$ and $3CoO,B_2O_3$.[44–6] The eutectic temperatures between B_2O_3 and $2CoO,B_2O_3$, $2CoO,B_2O_3$ and $3CoO,B_2O_3$, and $3CoO,B_2O_3$ and CoO were 900, 1080 and 1205°C, respectively.[44] A compound in the system was discovered, by examination of the previous work,[44] which had the peculiar property that it decomposed, on heating, into two immiscible liquids (see Fig. 46).[45] Two-layer formation is found in the system between 55% and 95·3% B_2O_3 (see Fig. 47).[44] On cooling the system it densifies at a very rapid rate by a solution-precipitation process in which the liquid wets the solid and penetrates easily between the grains that crystallize.[47]

Well-developed polarographic waves were obtained from cobaltous oxide, as is the case with many other oxides, in molten borax at 820°C.[7,8] Mixtures of this oxide in molten borax were studied, together with the system $2CoO,B_2O_3$–B_2O_3, to determine magnetic susceptibility values, which showed smaller maxima than equivalent measurements in the NiO–B_2O_3 glasses.[48] Antiferromagnetism has been studied in cobalt, iron and nickel borates.[49] The state of Co^{2+} ions in potassium borate glasses has been investigated.[50]

A 1:3 'cobalt borate' has been reduced with hydrogen at 750°C with 90% efficiency according to the equation $CoO,3B_2O_3 + H_2 \rightarrow Co + H_2O + 3B_2O_3$. At 500°C the efficiency drops to about 34%. The cobalt formed adsorbs hydrogen.[51]

$2CoO,B_2O_3$. A detailed investigation of the CoO–B_2O_3 system, using thermographic, micrographic and X-ray determinations, showed the presence of $2CoO,B_2O_3$ as a solid phase with a congruent melting point of 1150°C.[44] It has also been found present as a minor phase in the reaction between boric oxide, Co_3O_4, and cobaltous and sodium chlorides at 1000°C, in which the principal solid phase was cobalt ludwigite ($4CoO,Co_2O_3,B_2O_3$).[43] The compound is triclinic with a 2(2CoO -

B_3O_3) unit cell. The borate ion, $(B_2O_5)^{4-}$, is present, having a structure, based on a determination of interatomic distances, of the following form:



(Ref. 52)

The cobalt atom is hexa-coordinated to oxygen atoms in the form of a deformed octahedron.[52] It is isostructural with $2MgO,B_2O_3$ (triclinic modification) as are the corresponding manganese and ferrous compounds.[11]

$3CoO,B_2O_3$. If cobalt and boric oxides are heated together in a 3:1 ratio in a zirconia crucible, needle-like crystals of this borate form on cooling.[54] The compound is also found in the $CoO–B_2O_3$ system, in which its crystallization area has been determined by various physical methods.[44, 46]

The crystals are orthorhombic and isomorphous with the magnesium borate mineral kotoite ($3MgO,B_2O_3$).[54] A neutron diffraction study of $3CoO,B_2O_3$, synthesized from ^{11}B instead of ^{10}B because of the large capture cross-section of the latter, showed that it was antiferromagnetic below 37 K. Magnetic reflections have been indexed and the magnetic structure discussed.[55] The antiferromagnetism of this compound was also compared with that of manganese and nickel for 3:1 borates.[56] Its infra-red absorption spectrum has been studied.[57] The compound has BO_3 groups in its structure, and the cobalt ions have a coordination number of six (cf. $2CoO,B_2O_3$)[54]; on this basis the borate is placed in the 'order of insular non-ring borates with independent polyions'.[12]

$4CoO,B_2O_3$. By dissolving cobaltous oxide in alkali borates and cooling slowly, long needle crystals are obtained after leaching out the excess alkali borate with dilute nitric acid. The crystals are paramagnetic at room temperature and a unit crystal contains two $4CoO,B_2O_3$ units.[42]

Anhydrous Cobalt Borates Containing Other Elements

Of the alkali metals only lithium is known to form a mixed borate, $LiCoBO_3$, with cobalt. It may be prepared by heating equimolar quantities of cobaltous oxide and $LiBO_2$ at 770°C in an atmosphere of nitrogen; if an excess of lithium metaborate is used it can be prepared in contact with air at 1000°C.[58] A differential thermal analysis of the process has been carried out in conjunction with similar studies on lithium manganese and lithium zinc analogues.[59] X-Ray data for the borate, and its crystalline structure, have been investigated and shown to be similar to $3CoO,B_2O_3$.[58]

No Group II or Group III donor cobalt borates have been synthesized since Ebelmen and Mallard's work on magnesium cobalt borates (Mellor, V, 114), with the exception of the mixed metaborates of lanthanum or samarium, $CoLa(BO_2)_5$ is triclinic, $d\,(\text{expl.}) = 4{\cdot}2$.[120, 156] The structure has infinite chains of $[B_5O_{10}]^{5-}$ radicals composed of three B tetrahedra and two B triangles, and the preferred formula is $La_2Co_2[B_6B_4O_{20}]$. The compound $CoSm(BO_2)_5$ is orthorhombic, $d\,(\text{expl.}) = 4{\cdot}70$ and m.p. = 1080°C.[121] In Group IV, the compound CoO,SnO_2,B_2O_3, of dolomite structure[60, 61], has been synthesized and its stability discussed.[61, 62, 97] The cobalt analogues of vonsenite ($4FeO,Fe_2O_3,B_2O_3$) (*q.v.*), $4CoO,V_2O_3,B_2O_3$, $4CoO,Fe_2O_3,B_2O_3$ and $4CoO,Co_2O_3,B_2O_3$ have been prepared. The first of these is synthesized by electrolysis of a molten mixture of the constituents at 850–900°C.[20] By heating a mixture of Co_3O_4, cobaltous chloride, boric oxide and sodium chloride at 1000°C, $4CoO,Co_2O_3,B_2O_3$ is formed together with minor quantities of $2CoO,B_2O_3$ and cobalt boracite.[43] The structure of $4CoO,Co_2O_3,B_2O_3$ has been compared with that of natural ludwigite and the former's vanadium and ferric analogues.[43] The crystal structure of $CoFeBO_4$ has been determined.[110] The cobalt boracite is prepared by the standard method, entailing the volatilization of the components using a water-vapour, hydrogen-halide or hydrogen carrier at 300°C under pressure when the compound forms on a cold surface introduced into the pressure vessel.[28] The dielectric constants and piezoelectric properties between −100 and 370°C of cobalt boracites $5CoO,CoX_2,7B_2O_3$ (where $X = Cl$, Br, I) have been determined.[53, 63] The dichoism and birefringence in the cobalt-iodine boracite are about three orders of magnitude lower than in the nickel-iodine analogue.[96]

As with many other bivalent metals, cobalt also forms $Co(B_2O(OCOCH_3)_5)_2$ from diboron oxide tetra-acetate and cobalt acetate.[4]

Hydrated Cobalt Borates

The only simple hydrated cobalt borates with a well-defined crystalline structure are $CoO,3B_2O_3,8H_2O$ and $CoO,3B_2O_3,10H_2O$. Other borates of varying $CoO:B_2O_3:H_2O$ ratios are obtainable as powders by reaction of a cobalt salt with a solution of borax, the ratio depending on the molar ratio of the metal salt to borax, the temperature and the concentration.[64] A fairly well-defined 1:1 borate is formed when equimolar quantities of cobaltous chloride solution (0·1M) react with a borax solution (0·1M). The precipitate separated from this reaction mixture is an amorphous pink powder having a hydration of $3H_2O$ when fresh but changing to $2H_2O$ on ageing.[65–6] The formation of CoO,B_2O_3,nH_2O has been postulated as the cause of the change of structure of the double layer causing polarization of a cobalt-plated cathode when boric acid is added to the cobaltous sulphate electrolyte.[67]

$CoO,3B_2O_3,8H_2O$. As with other 'hexaborates' of alkaline earths and heavy metals the cobalt hexaborate may be prepared by heating a solution of cobalt acetate with boric acid in the stoichiometric proportions. The reaction is slow and depends on the evaporation of acetic acid, the borate replacing the volatile acetate radical.[64] This procedure can be accelerated and reduced to a one-stage process by a reaction according to the following equation:

$$CoCl_2 + Na_2B_4O_7 + nH_3BO_3 + xH_2O \rightarrow CoO,3B_2O_3,8H_2O + 2NaCl + (n-2)H_3BO_3 + (x-5)H_2O.$$

The crystals are not formed immediately, the first precipitate having a 3:1 $CoO:B_2O_3$ ratio; this precipitate transforms on stirring for 1–2 days into $CoO,3B_2O_3,H_2O$ and may be isolated as a friable pink powder.[64] This borate loses 2 molecules of water of crystallization at 50°C and therefore must be dried at low temperatures. Above 50°C the hexahydrate is stable until 105°, but extremely hygroscopic; between 105° and 150°C it is not hygroscopic but loses 4 molecules of water. The last 2 molecules of water are lost at about 450°C. The compound has a density of 2·0 and is decomposed in water, but dissolves to the extent of 5 g/l in a 3% boric acid solution and 7 g/l in a 5% boric acid solution without hydrolysis.[64] The 7·5 hydrate is believed from D.T.A. curve evidence to be a solid solution.[105–6] A study of the thermal decomposition of bivalent iron and cobalt hexaborates has been carried out.[93] The mobility of the anion of a solution of the borate in 3% boric acid is 16·2 mho/cm^2 at 25°C.[68] Infra-red absorption spectra have been determined.[107]

$CoO,3B_2O_3,10H_2O$. A recent study of the preparation and properties of this hydrate has been reported.[95] Its structure is composed of sub-units of $Co(H_2O)_3$-$[B_6O_7(OH)_6]$.[117] Thermal decomposition has been studied.[115]

Hydrated Cobalt Borates Containing Other Elements

Ammines have been formed with the borate in the anion and cation. If the compound $[Co(NO_3)_3NH_3)_3]$ is reacted with sodium metaborate solution at 45°C, ammonia is evolved. On cooling the solution a purplish-grey precipitate is formed which is very slightly soluble in water (0·3 g/l), having the formula $Na_2[Co(BO_2)_5NH_3]$, i.e. sodium cobaltiammonioborate.[69] To obtain a product which has a cation containing the borate radical, the ammine hydroxide $[Co(H_2O)(NH_3)_5](OH)_3$ is treated with boric acid at 70–100°C, when $[Co(BO_2)(NH_3)_5]Cl_2$ is formed with the exchange of the hydroxyl groups for chloride.[70] In addition to these ammines a well-defined ammonium cobalt borate, $(NH_4)_2O,CoO,6B_2O_3,11H_2O$ has also been synthesized. Solutions of ammonium hydroxide, boric acid and cobalt chloride are mixed together in 20:9:5 molar ratios and agitated vigorously, precipitation thus being avoided. On keeping the solution for 1 day a crop of crystals of $(NH_4)_2O,CoO,6B_2O_3,11H_2O$ is obtained. It has a density of 1·96 and is decomposed by water. It decomposes, losing 8 molecules of water and all the ammonia, at 150–200°C, but needs to be heated at 450°C before losing the remaining $3H_2O$.[64] The potassium analogue of the above ammonium salt is formed in exactly the same manner by substituting potassium hydroxide for ammonium hydroxide as one of the reactants.[64] The compound $K_2O,CoO,6B_2O_3,11H_2O$ crystallizes well at pH 7–8 but at pH 6·0, $CoO,3B_2O_3$,aq. is formed, and above pH 8, CoO,B_2O_3,nH_2O precipitates.[71] The crystal structure of potassium-cobalt hexaborate has been determined as $K_2Co[B_6O_7(OH)_6]_2,4H_2O$.[118–19] It is triclinic.

NICKEL BORATES

Anhydrous Nickel Borates

The NiO–B_2O_3 system has been studied and found to have the common characteristic of many metal-borate systems of forming an extensive two-liquid region. This immiscibility covers the range 1·64–59·5 wt.-% NiO; on cooling, $2NiO,B_2O_3$ crystallizes from the lower layer.[72]

The systems $Na_2O,2B_2O_3$–NiO, $K_2O,2B_2O_3$–NiO, and $Rb_2O,2B_2O_3$–NiO have been studied in the range 700–1200°C. All show simple eutectic properties with eutectic temperatures and component percentages, respectively, as follows: 735 ± 5°C, 3 mol.-% NiO; 788 ± 4°C, 4 mol.-% NiO; 710 ± 5°C, 2 mol.-% NiO. The phase boundaries between liquid and liquid + NiO fields have been experimentally determined and compared with the calculated values, and found to be nearly theoretical except for the $Na_2O,2B_2O_3$–NiO system, which deviated slightly.[73] Another worker has obtained $2NiO,B_2O_3$ and $3NiO,B_2O_3$ by cooling a Na_2O–B_2O_3 system containing NiO.[72]

In common with other oxides, nickel oxide in molten borax at 820°C shows well-developed polarographic waves.[8] Chemical polarization occurs during electrolysis.[7] Nickel borates as well as magnesium and zinc borates have been used to the extent of 0·6% as condensing agents in the reaction between phenols and formaldehyde.[74]

$2NiO,B_2O_3$. This borate crystallizes, as mentioned above, from the NiO–B_2O_3 and NiO–Na_2O–B_2O_3 systems. It may be prepared more specifically by fusing equimolar quantities of nickel sulphate and borax in a platinum crucible for 2 hours at 800°C, cooling and leaching out the excess sodium borate with concentrated hydrochloric acid. The crystals produced can be reduced by hydrogen at 450–610°C to give nickel, in a form capable of adsorbing hydrogen. A lower oxide of boron is not formed under these conditions.[75]

$2NiO,B_2O_3$ has been shown to be paramagnetic.[42]

$3NiO,B_2O_3$. Like the 2:1 compound, $3NiO,B_2O_3$ is formed as a solid phase in the NiO–Na_2O–B_2O_3 system.[72] Green needle- and lamina-type crystals have been obtained from nickel boracite melts. The crystal parameters are in close agreement with magnesium and cobalt 3:1 borates. The space-group has been determined; it corresponds with a rhombic bipyramidal structure.[76] Crystal structure was refined in later work.[122]

The infra-red spectrum of $3NiO,B_2O_3$ varies, according to whether the borate has been freshly prepared or kept.[77] Antiferromagnetism has been studied, especially in the 3:1 borates of manganese, nickel and cobalt.[49]

$4NiO,B_2O_3$. Like the cobalt and cupric borates, nickel also forms a 4:1 borate. By dissolving nickel oxide in alkali borates and slowly cooling, long needles of the 'boroferrite' crystallize. Its lattice parameters have been determined.[42]

Anhydrous Nickel Borates Containing Other Elements

Nickel boracites, $5NiO,7B_2O_3,NiX_2$ (where X = Cl, Br and I) have been prepared by using the vapour-phase method mentioned elsewhere (especially under magnesium borates)[28] and also by hydrothermal methods.[98] Very pure single crystals of $5NiO,7B_2O_3,NiI_2$, up to 10 mm in their longest dimensions, have been grown by a chemical transport method.[78] Sector growth and twinning of nickel boracites has been studied.[79] Dielectric constants and dielectric losses have been measured at 100–370°C and between 50 kHz and 50 MHz (cf. cobalt boracites), and showed some anomalies. The piezoelectric properties were studied during this investigation.[80] The ferromagnetic behaviour has been studied at temperatures below 64 K.[78, 79] Rotation diagrams showed a slight hexagonal component in the (111) plane of the crystals. In the (100) plane, however, large tetragonal torsion moments were recorded having frequency discontinuities. This behaviour can be only partly explained on the basis of ferromagnetic domain-wall motion.[78] The temperature dependence of the paramagnetic susceptibility of the nickel iodo-boracite has been investigated.[82, 83] Nickel iodide boracite has cubic symmetry above 120 K and shows intrinsic optical anisotropy at room temperature.[99] Another study of the optical anisotropy of this compound showing the relation to quadrupole transitions has been made.[100] The structure is the same as that of β-magnesium boracites.

Magnetic susceptibilities have been determined for the nickel analogue of ludwigite $4NiO,Fe_2O_3,B_2O_3$[16, 109] in the range 0–1100°C; above 1100°C the compound decomposes. $Fe_2O_32NiOB_2O_3$, which has a warwickite structure, has been prepared by hydrothermal synthesis at very high pressure.[108] Both NiO,SnO_2,B_2O_6 and NiO,TiO_2,B_2O_3, which have dolomite structures, have been synthesized[60, 61]; the latter forms a series of solid solutions with BaO,SnO_2,B_2O_3.[61] Their stabilities have been discussed.[61] The structure of $5NiO,TiO_2,B_2O_3$ was determined by single-crystal X-ray analysis.[111] The compound is orthorhombic, with the same structure as ludwigite.

Hydrated Nickel Borates

Amorphous borates of various compositions are formed by the action of a nickel salt on borax solutions, the $NiO:B_2O_3$ ratio of the product depending on the exact conditions of the reaction.[64] Manganese, cobalt and nickel all form octahydrated 1:3 borates. The cobalt compound is the only truly crystalline borate, but nickel forms another well-defined crystalline 1:3 borate hydrate. Complex salts containing tetra- and hexa-amminated nickel ions are easily formed, and it is suggested that 6 of the molecules of water of crystallization in $NiO,3B_2O_3,8H_2O$ form a complex ion with the nickel, $[Ni(H_2O)_6]^{2+}$ which may be substituted by ammonium molecules with comparative ease.[85]

The compositions of sparingly soluble compounds precipitated by alkali from solutions of nickel salts in the presence of boric acid have been determined.[86] When nickel sulphate is titrated with sodium hydroxide in the presence of boric acid, a complex borate $x NiSO_4,y Ni(OH)_2,z H_3BO_3$ is formed, which refutes the theory that the boric acid is present only as a buffer. A relationship between pH and the boric acid concentration was found.[87]

$NiO,3B_2O_3,8H_2O$. In contrast to the other heavy metal hexaborates, $NiO,3B_2O_3,8H_2O$ could not be prepared by displacing acetic acid from nickel acetate and substituting the borate group.[64] A precipitate ($2NiO,3B_2O_3,xH_2O$) formed from equivalent quantities of a nickel salt and borax, in decinormal or greater concentrations, may be dissolved in a supersaturated boric acid solution, from which, over a period of 2–3 days, the 1:3:8 borate crystallizes. Alternatively, it may be formed in an analogous fashion to the corresponding manganese and cobalt hexaborates. Equimolar quantities of a nickel salt and $Na_2O{:}4B_2O_3$ solution are mixed slowly with stirring; after 2–3 days of continual stirring a 60–70% yield of $NiO,3B_2O_3,8H_2O$ is obtained as thin hexagonal platelets. The manganese and cobalt hexaborates are isomorphous, but the nickel hexaborate differs somewhat.[64]

The density is 1·70, and on fusing it forms a very hard glass. It hydrolyses in water and is slightly soluble in boric acid solutions. All the water of crystallization is lost at 100–160°C showing that it is weakly held even in the postulated hydrated nickel ion.[64] Thermal decomposition leads to amorphous (at 500°C) and crystalline (at 680°C) anhydrous products.[113–15] Kinetic parameters were measured.[116]

$NiO,3B_2O_3,10H_2O$. This hydrate is not stable in an aqueous solution at room temperature, and is prepared by dissolving the 1:3:8 borate in 3% boric acid solution and adding alcohol at a temperature not above 10°C. If the alcohol is added very slowly (during hours) the crystals can be grown longer.[64]

$NiO,B_2O_3,2H_2O$. This compound is obtained as a finely dispersed solid phase from the aqueous reaction of $NiCl_2$ with an alkali-metal tetraborate, optionally with the addition of NaCl or KCl.[112]

$NiO,B_2O_3,5H_2O$. By hydrolysing the $NiO,3B_2O_3,8H_2O$ in a 0·5% solution of boric acid at 80°C a light-green crystalline powder is formed. This powder has a density at 25° of 2·09, but no good crystals have been formed. The water of crystallization is lost over the range 50–450°C.[64] Its structure has been determined.[117]

Amminated Nickel Borates. By adding borax to a solution of nickel sulphate in concentrated ammonia at 80–90°C and cooling in an atmosphere of ammonia, bluish crystals of $[Ni(NH_3)_4]B_4O_7,4H_2O$ are formed. Prolonged storage of this compound in ammonia gas causes the absorption of two more molecules of ammonia, which are lost in air storage. All ammonia is lost by heating to 160–170°C.[85]

If $NiO,3B_2O_3,8H_2O$, alternatively written $[Ni(H_2O)_6]B_6O_{10},5H_2O$ is exposed to ammonia for some 25 days in the presence of potassium hydroxide $[Ni(NH_3)_6]B_6O_{10},5H_2O$ is formed. It loses 2 molecules of ammonia at 105°C and the rest at 170°C.[85]

A double salt of the hexammine with an ammonium 1:2 borate is formed variously by reacting together ammonia, boric acid and nickel hydroxide, or by substituting one of the amorphous nickel borates for the hydroxide, or by simply reacting the hexammine $[Ni(NH_3)_6]B_6O_{10},2H_2O$ with ammonia 1:2 borate in solution.[85]

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SECTION A13

BORON–OXYGEN COMPOUNDS OF ELEMENTS OF GROUPS V AND VI

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This section considers various aspects, including preparation, properties and applications, of the boron–oxygen compounds of the metals of Groups V and VI. By far the most important of these compounds is boron phosphate, which has been extensively studied in view of its potential technological importance. Much of the work relating to this material, and to the borophosphates, has been reported only in the patent literature, and this has been drawn on extensively where no other published data are available.

The boron–oxygen compounds of arsenic and vanadium have been the subject of less investigation, while compounds of bismuth, niobium, tantalum, chromium and uranium are rather scantily reported. The boratosulphates, borotungstic acids and borotungstates have been described in somewhat greater detail, but very little information relating to applications is available from published work.

BORON PHOSPHATE

Preparation

The preparation of boron phosphate by the reaction of boric acid with orthophosphoric acid in stoichiometric proportions, followed by dehydration at temperatures up to 1200°C, has been reported by a number of authors[1–9, 256]:

$$H_3BO_3 + H_3PO_4 \rightarrow BPO_4 + 3H_2O$$

Two patents[1, 3] describe the dehydration of the intermediate products at temperatures of 100°C and 100°–150°C, respectively, but the final products of these preparations would certainly contain combined water. Other patents[2, 4, 8] specify dehydration temperatures up to 350°C; one[9] uses the range 400°–500°C, whilst another[5] employs calcination at 600°C, but these preparations would also leave some combined water in the final product. Complete dehydration requires temperatures of at least 1000°C, and preparations using temperatures of this order have been patented[6] and have also been described by other authors.[7]

A method of preparation of boron phosphate using an excess of phosphoric acid and a final ignition temperature of 350°C has been described.[10] Since this temperature is insufficient to volatilize the excess of phosphoric oxide, the product obtained would be non-stoichiometric in addition to retaining some combined water.

Giorgini et al.[11–13] have studied the preparation of boron phosphate from boric and phosphoric acids under various conditions. Under aqueous conditions the rate-determining steps are the rate of reaction and the rate of diffusion of water through the product layer. A similar result was reported by Baccaredda.[14] Levi and Gilbert[15] state that when the P_2O_5 content of the system B_2O_3–P_2O_5–H_2O exceeds 48% the solid in equilibrium with the solution is boron phosphate. In a more recent study at 15 and 90°C, Russian workers found that at the higher temperature and at 0–45·5 wt. % P_2O_5 only H_3BO_3 separated as a solid phase, but that at higher P_2O_5

concentrations solid BPO_4 separated along with solid H_3BO_3.[257] At 15°C, H_3BO_3 was the only solid phase.

Boron phosphate has also been prepared[16–17] by the reaction of orthophosphoric acid with boric oxide, metaboric acid or orthoboric acid suspended in xylene or other organic media, with subsequent elimination of water by azeotropic distillation.[18] The granule size of the product depends on the following factors: boric acid type and its concentration in the organic medium, the feed rate of the orthophosphoric acid, the nature of the organic medium, and the stirring rate.

Boron phosphate may also be prepared by the reaction of boric oxide with syrupy phosphoric acid, followed by evaporation to dryness[19], and by the reaction of boric acid with phosphorus pentoxide at temperatures below 400°C to give an intermediate product which is then ignited at red heat.[20] It is again formed when phosphorus pentoxide is added in small amounts to an equivalent proportion of fused boric oxide at 600°–650°C.[21] This reaction is exothermic and the melt solidifies to give boron phosphate on cooling. In another method[22] boron phosphate is prepared from equimolar proportions of boric oxide and phosphorus pentoxide heated in a muffle furnace at 1000°C, unreacted material being removed subsequently by washing with water.

Boron phosphate can be prepared from starting materials other than boric and phosphoric acids or their anhydrides. Levi and Ghiron[23] heated diammonium hydrogen phosphate with boric acid, eventually under vacuum to eliminate all traces of ammonia, to obtain boron phosphate:

$$(NH_4)_2HPO_4 + H_3BO_3 \rightarrow BPO_4 + 2NH_3 + 3H_2O$$

A similar process has been patented[24] as a method for the production of a catalytically active form of boron phosphate.

Boron phosphides are oxidized when heated in the presence of oxygen to form boron phosphate.[25–7] The black modification of boron phosphide oxidizes very slowly at temperatures above 650°C but more rapidly at 815°C, while the maroon form is oxidized rapidly above 620°C.[26]

Dihydroxyfluoroboric acid reacts with phosphorus pentachloride or pentabromide to form boron phosphate, boron trifluoride and the corresponding phosphorus oxyhalide and hydrogen halide[28]:

$$3H_3BO_2F_2 + 3PX_5 \rightarrow BPO_4 + 2BF_3 + 2POX_3 + 9HX$$

Dihydroxyfluoroboric acid also reacts with phosphorus pentoxide to give boron phosphate, hydrogen fluoride and water[28]:

$$2H_3BO_2F_2 + P_2O_5 \rightarrow 2BPO_4 + 4HF + H_2O$$

Cherbuliez and co-workers[29] studied the reaction of triethyl borate with phosphoric acid under different conditions and found that in each case boron phosphate is formed. Equimolar amounts of triethyl borate and orthophosphoric acid were heated under reflux for 10 min, cooled and filtered; the residue was washed with diethyl ether to give a form of boron phosphate which is readily soluble in water. When triethyl borate and orthophosphoric acid are heated on a water bath, a solid corresponding to a mixture of the ethoxyborophosphoric acids, $(PO_4H_2)_2BOEt$ and $[(PO_4H_2)_2B(OEt)_2]H$, with boron phosphate, is formed. The ethoxyborophosphoric acids react slowly at elevated temperatures with triethyl borate to yield boron phosphate. Orthophosphoric acid when dissolved in ethanol and heated under reflux for 3 h with triethyl borate gives a voluminous precipitate of boron phosphate, which may be recovered by washing with diethyl ether and drying in air. Boron phosphate is also prepared[30] by refluxing triethyl borate and orthophosphoric acid; annealing the product at 750°C gives crystalline aggregates.

A patented process[31] describes the formation of a boron phosphate gel by the reaction of a trialkyl borate (the alkyl groups each having at least two carbon atoms) with phosphoric acid solution in a heated zone, and removing the alkanol formed as a by-product. Boron phosphate may also be prepared[32] by the reaction of triethyl phosphate, $(EtO)_3P{:}O$, with boron trichloride at -70°C to form a complex which, when heated above 55°–60°C, evolves ethyl chloride. The residue is then heated successively at 100°C, 180°C and 300°–320°C under reduced pressure, and finally ignited in air at 1000°C to obtain crystalline boron phosphate.

It has been reported[33] that boron phosphate is present to the extent of 4½% in deposits taken from the heating side of the fuel economizer of a steam boiler.

Structure

According to Schulze[34–5] boron phosphate has a structure of low-cristobalite form, each boron and phosphorus atom being surrounded tetrahedrally by oxygen atoms, each oxygen atom belonging to two tetrahedra. The lattice constants given are: $a=4{\cdot}322$, $c=6{\cdot}640$ Å; there are two molecules per unit cell. However, Levi and Ghiron[23] give values for the lattice constants of 4·46 and 6·79 Å, respectively.

The structure of boron phosphate when subjected to high pressures and temperatures has been extensively studied.[36–40] Shafer and co-workers[36] found that boron phosphate changes from cristobalite form to a quartz form with increasing pressure; this transformation occurs at 46,000 bars.[37] Dachille and Dent Glasser[38] carried out single-crystal studies of a high-pressure form of boron phosphate and quote unit cell dimensions of $a=4{\cdot}470$ and $c=9{\cdot}926$ Å. The structure, which contains three molecules per unit cell, is derived from the quartz structure by doubling the c-axis. The calculated density of this form of boron phosphate is 3·069 g cm^{-3} and the experimental value 3·05 g cm^{-3}. Mackenzie and co-workers[39] prepared boron phosphate at 1000°–2000°C under a pressure of 85,000 atm and found it to have a hexagonal structure with unit cell dimensions of $a=7{\cdot}75$ and $c=9{\cdot}95$ Å, with nine molecules per unit cell. The density of this material was found experimentally also to be 3·05 g cm^{-3}.[39] The transformations of boron phosphate at high pressures and temperatures have been reviewed by Tomonari.[41]

Physical Properties

Boron phosphate was found to be thermally stable up to about 1450°C, at which temperature it begins to vaporize, probably without decomposition.[42] The linear coefficient of thermal expansion (per °C) of boron phosphate over the range 25°–1000°C is 9×10^{-6}. Heat capacity data for boron phosphate up to 927°C have been published.[43] Boron phosphate is sufficiently stable at temperatures in excess of 1000°C for material calcined at this temperature to be used as the final product in the thermogravimetric determination of boron.[44] A transpiration study of boron phosphate at high temperatures has been made[45], and the effect of heat on boron phosphate has been studied by X-ray diffraction, differential thermal analysis and vapour effusion techniques.[46]

The heat of formation of boron phosphate in the reaction:

$$BP(\text{cryst.}) + 2O_2(\text{gas}) \rightarrow BPO_4(\text{cryst.})$$

is $\Delta H_{208} = -224{\cdot}9 \pm 4{\cdot}7$ kcal mole^{-1}.[27] Low-temperature heat capacities and derived thermodynamic functions have also been reported.[47]

Dachille and Roy[48] obtained an infra-red spectrum for boron phosphate, while the n.m.r. spectra and quadrupole coupling constant ($50{\cdot}4 \pm 0{\cdot}5$ kHz) of ^{11}B in boron phosphate have been obtained by Bray and co-workers.[30, 49] Inelastic light scattering was used to probe phonon behaviour in BPO_4.[258]

Chemical Properties

Gruner[50] states that boron phosphate forms tri-, tetra-, penta- and hexahydrates which, on extraction with liquid ammonia, form $BPO_4,3H_2O,NH_3$. This he explains by considering the trihydrate as an acid of the type RH_2, where R is:

The ammonia addition compound is, therefore, a salt of the type RNH_4H, whilst the tetra-, penta- and hexahydrates are respectively RH_2,H_2O, $RH_2,2H_2O$ and $RH_2,3H_2O$.

Freidlin and co-workers[51] studied the dehydration of hydrated boron phosphate containing 9·5% of water (less than is required for a monohydrate) and showed that 8% is easily removed by heating but the last 1·5% is more tightly bound. This residual water may be removed at temperatures in excess of 450°C, and the boron phosphate is completely dehydrated at 800°C. Very similar results were obtained by Baccaredda and co-workers[14] and by Ashboren.[256] None of these workers reports the formation of a definite hydrate, but Russian research has revealed a trihydrate after calcination at 300°C.[255]

All the hydrates of boron phosphate hydrolyze in aqueous solution to give boric and phosphoric acids.[50, 257] A similar result was obtained for the hydrolysis of anhydrous boron phosphate by Baccaredda and co-workers[14], who also studied its alcoholysis. The stability of boron phosphate to hydrolysis and alcoholysis increased as the calcination temperature increased; the rate of alcoholysis may be used to determine the amount of uncombined boric oxide. Giorgini et al.[13] studied the hydrolysis of boron phosphate containing different $P_2O_5:B_2O_3$ molar ratios calcined at temperatures in the range 200°–600°C. These workers also found that the stability of boron phosphate to hydrolysis increases as the calcination temperature increases, but in addition they found that hydrolysis increases as the P_2O_5 content increases. The adsorption of water by boron phosphate samples pre-heated to temperatures of 100°C, 200°C or 300°C has also been studied by Moffat and co-workers.[52, 278–80] Their kinetic studies suggested that, on average, two hydrogen bonds per H_2O are involved in the adsorption; subsequent infra-red spectroscopic work detected bands assignable to BOH and POH.[280] They also examined the adsorption of krypton[281] and argon.[282]

Boron phosphate decomposes to form the free acids when refluxed with ethyl alcohol[29], but it is stated elsewhere[22, 53] that on refluxing with alcohols such as *n*-octyl alcohol a boron phosphate ester is formed.

Boron phosphate forms gels in concentrated sulphuric acid and oleum which increase in firmness with concentration; equimolar proportions of the two acids give the best results.[54] Gels formed at 25°C are faintly opalescent, while those formed at 100°C are more strongly opalescent. All gels display slight syneresis, but there is little indication of thixotropic properties.

Hummel and co-workers[55–7] have studied boron phosphate–oxide systems. The BPO_4–SiO_2 join of the B_2O_3–SiO_2–P_2O_5 system forms its lowest melting mixture at approximately 62% SiO_2, the m.p. of this mixture being 975 ± 25°C. The thermal expansion and refractive indices of glasses along the join were determined. The system B_2O_3–SiO_2–P_2O_5 is not a true ternary at atmospheric pressure and temperatures below 1400°C because of the tenacious retention of water. If the presence of water is neglected, BPO_4 is a primary phase over a considerable area of the triangle B_2O_3–BPO_4–SiO_2. Ternary compounds, unstable at temperatures greater than 710°C and having the probable compositions $22Li_2O,11B_2O_3,13P_2O_5$ and $2Li_2O,3B_2O_3,$-P_2O_5, were formed with difficulty in the $LiPO_3$–BPO_4 and $Li_4P_2O_7$–BPO_4 systems. Glasses formed in these systems have poor chemical durability. Ray et al.[260] have recently characterized borophosphate glasses containing about 70 mol-% P_2O_5 and up to 5 mol-% B_2O_3. Some of them were an order of magnitude more stable to water than corresponding simple phosphate glasses.

The addition of 0·5 to 1·5% of boron phosphate to alumina powder has been found greatly to retard its sintering.[58]

Hund[59] has described heterotypic mixed phases in which boron phosphate is the host lattice, and gives spectral emission curves for NiO–As_2O_5, CoO–As_2O_5 and CuO–V_2O_5 in boron phosphate. Compounds of this type, said to be useful for pigments, fillers or catalysts, have been patented.[60–61]

Electrolysis of boron phosphate in melts containing alkali metal fluorides results in the formation of boron phosphide, BP.[62] Boron phosphate may be reduced to the elements by ignition with aluminium if a primer of potassium or sodium nitrite and calcium silicide is used.[63]

Applications as Catalysts

Boron phosphate has been used, or proposed, as a catalyst for a wide range of reactions falling within a number of different categories which are considered in detail below.

DEHYDRATION

Freidlin and co-workers[7, 51, 64–5] studied the use of boron phosphate as a catalyst in the dehydration of alcohols, with particular reference to the relationship of its catalytic activity to the conditions under which it was prepared. The maximum activity of boron phosphate catalysts with respect to dehydration of amyl alcohol to pentanes and isomerization of 1-pentane was obtained by preparing the catalysts at 600°C. These workers[66] also studied stereospecificity in the dehydration of 3-pentanol in the presence of boron phosphate, among other catalysts, and found the yield of pentenes to reach approximately 80% at a temperature of 260°C; the *cis*:*trans* isomer ratio was 1·0.

Boron phosphate has been used as a catalyst in the dehydration of hydroxylated oils[67] at 240°–260°C to form drying oils. It has also been used[68] in the dehydration of N-alkyl-substituted amides, the substituents having hydrogen atoms in the α-position, at 360°–410°C to form a nitrile group and an olefinic bond. ω-Cyano carboxylic acids may be prepared[69] by heating an aliphatic dicarboxylic diamide with the free dicarboxylic acid under reduced pressure at 250°–300°C over a boron phosphate catalyst.

The use of boron phosphate as a dehydration catalyst has been widely exploited for the preparation of nitriles. A specific example is the reaction of adipic acid with ammonia to form adiponitrile.[70–72] It is recommended that a molecular excess of ammonia be used at a temperature in the range 300°–550°C.[70] Adiponitrile may also be prepared by the reaction of δ-cyanovaleramide with ammonia over a boron phosphate catalyst.[73–4] ω-Aminonitriles are made by contacting a mixture of ammonia and a lactam with boron phosphate at a temperature in the range 250°–450°C[75] whilst decane-1,10-dicarbonitrile is made by the reaction of 11-cyanoundecanoic acid with ammonia at temperatures in the range 300°–450°C.[76] Carboxylic acids react with excess of ammonia in the presence of superheated steam over a boron phosphate catalyst at 260°–500°C to give corresponding mononitriles and dinitriles.[77]

The catalytic dehydration of acetamide vapour at 230°–450°C over boron phosphate to yield acetonitrile has been patented.[78] Acetonitrile, together with hydrogen cyanide, is also the product of the reaction of acetone, ethyl formate or methyl acetate with air and/or oxygen and ammonia over a boron phosphate catalyst at temperatures in the range 300°–600°C.[79]

Unsaturated aliphatic nitriles, such as acrylonitrile and methacrylonitrile, may be prepared using boron phosphate catalysts to which compounds of various metals are added in the proportion of 1 to 10% as activators.[80] The use of boron phosphate as a catalyst in the preparation of dinitriles from the corresponding acid amide has been patented[81]; in this reaction the yield of dinitrile is increased if the boron phosphate is heated for 3–4 h at 350°C in an atmosphere of ammonia before use. Nitriles are also prepared by oxidizing methyl benzenes or methyl naphthalenes with air or oxygen at 300°–600°C in the presence of ammonia and a metal oxide catalyst which may be supported on boron phosphate.[82]

Other examples of the use of boron phosphate as a dehydration catalyst are the decomposition of 4,4-dimethyl-*m*-dioxan to isoprene[5, 83] and the formation of piperylene from tetrahydrofuran, butylene from butanol and butadiene from 1,3-butanediol.[2, 4] Boron phosphate also catalyzes the dehydration of methyltetrahydrofuran to give a mixture of trans- and cis-1,3-pentadiene[84], and of *bis*-carbinols to give the corresponding *m*- and *p*-isopropenylphenyl-dimethyl-carbinols[85], the reaction being stopped after the dehydration of one carbinol group. Equimolar mixtures of 1,10-dicyanodecane and dodecanedioic acid are obtained by high-temperature disproportionation of 11-cyanoundecanoic acid in the presence of boron phosphate.[86]

Boron phosphate used as a dehydration catalyst may be regenerated by heating in a current of air at 400°–600°C.[4]

AMINATION

The influence of experimental conditions on the activity of a boron phosphate catalyst in the amination of methanol has been studied systematically.[87–8] It was found that the yield is influenced primarily by the temperatures used, which were in the range 300°–400°C, while the ratio of mono- to trimethylamine is governed by the excess of ammonia used.[87] The activity of the catalyst decreased sharply with time at 360°C, whilst at 400°C there was little or no decrease in activity.[88]

Patented processes utilize boron phosphate as a catalyst in the preparation of diphenylamine from aniline and a halogen[89], the production of melamine from hydrogen cyanate and ammonia[90–91], and the preparation of N,N-diethyltoluamides from diethylamine and toluic acid at 250°–350°C.[92]

Boron phosphate catalysts used in the production of melamine may be regenerated by treatment with superheated steam at temperatures in the region of 400°C.[91]

POLYMERIZATION AND ISOMERIZATION

Boron phosphate has been used as a catalyst for the polymerization of formaldehyde and acetaldehyde.[24] In each case the process is carried out at $-70°C$ *in vacuo* for an extended period. Aliphatic mono-olefins may also be polymerized in the presence of a boron phosphate catalyst, which may be used alone or supported on an inert metal-oxide carrier.[93] Conversions to polymer of 40–100% are achieved at temperatures in the range 60°–315°C under pressures up to 1000 lb in^{-2}. Boron phosphate does not catalyze the polymerization of ethylene oxide[94], but may be used as a catalyst in the polymerization of mono-epoxides.[95]

Boron phosphate has been used[10] as a catalyst for the isomerization of straight-chain olefins to branched-chain olefins at temperatures between 350°C and 600°C. Other applications in which boron phosphate is used to catalyze the isomerization of aliphatic olefins have been patented.[8, 96–8] In two of these patents[8, 98] the catalysts were prepared with an excess of phosphoric acid, which would leave free phosphorus pentoxide in the final product at the preparation temperatures used.

Alkyl vinyl ethers give good yields of monomeric aldehydes when passed over a boron phosphate catalyst at temperatures in the range 150°–400°C.[99] Careful control of the reaction temperature is required to obtain optimum yields. Boron phosphate may be used as a catalyst for an ester-interchange reaction which yields linear polyesters from ethylene glycol and dialkyl esters of terephthalic acid or a dibasic carboxylic acid.[100]

OTHER CATALYTIC APPLICATIONS

Boron phosphate has been used, in conjunction with alumina, as a catalyst for the desulphurization of hydrocarbons.[3] It has also been used for the de-alcoholization of β-alkoxy or -aryloxy monocarboxylic acid esters to form unsaturated monocarboxylic acid esters.[101] This reaction is preferably carried out under reduced pressure at 210°–240°C. Other reactions catalyzed by boron phosphate include the nitration of aromatic hydrocarbons[102] and the production of conjugated diolefins.[103]

It has also been used as a catalyst for the reaction of steam, carbon monoxide and olefinic hydrocarbons to form acids[104], and for the reaction of olefins with molecular oxygen at elevated temperatures.[100, 105] Unsaturated aldehydes and acids may be made from propylene or isobutene by this method, using a reaction temperature in the range 300°–500°C.[106]

Boron phosphate has been used as a catalyst in dehydrochlorination reactions in the production of alkylates[107] and mono-olefins.[108] Patented processes for the preparation of pyridine and substituted pyridines also describe the use of boron phosphate as a catalyst[109–12], as do those for the preparation of methylenimines, including caprolactam[113–14], and the conversion of anatase to rutile.[115] Its use as a catalyst for the chlorination of mixtures of paraffins to monochlorides has been patented.[116]

The preparation of 2-butanol from 2-butene over a boron phosphate catalyst at elevated temperatures and pressures has been reported[117], as has the conversion of triethoxybutane to ethoxybutadiene.[118] The gas-phase hydration of ethylene at 290°–360°C has been studied.[253] Giorgini and co-workers also made extensive studies of boron phosphate as a catalyst of the vapour-phase hydration of acetylene and other unsaturated hydrocarbons.[12, 123–7] They found that the highest values of the conversion of acetylene to acetaldehyde are obtained at high temperatures, but that at high temperatures the activity of the catalyst decreases with time at the greatest rate. Optimum conditions for the reaction were found to occur over the temperature range 440°–500°C. Use of catalyst materials made from mixtures containing excess of phosphoric acid showed that products containing excess of phosphorus pentoxide have higher catalytic activity than stoichiometric boron phosphate.

Laboratory studies have been carried out by Freidlin and co-workers[119] on optimum conditions for the synthesis of guaiacol from pyrocatechol and methanol using a boron phosphate catalyst. When a molar ratio of pyrocatechol to methanol of 1:6 was used at a temperature of 300°C, a yield of 50–60% of guaiacol was obtained and the catalyst remained active for 30–40 h. The same workers[120] also studied the synthesis of *o*-ethoxyphenol from pyrocatechol and ethanol over a boron phosphate catalyst. Other laboratory studies[121] include boron phosphate as a catalyst for the reaction of benzene with dimethyl ether to form toluene, and as a catalyst for the hydration of ethylene.[122]

Boron phosphate may also be used in combination with alumina, silica, molybdenum and cobalt to form stable catalysts which may be used in both cracking and hydrogenation reactions[128], and as a support for aluminium phosphate to catalyze reactions leading to the formation of alkylated benzene hydrocarbons.[129] Benzene and ethylbenzene may be prepared by hydrogenation of the products of reaction of toluene and sulphur over a catalyst incorporating boron phosphate.[130]

Alkyl- or aryl-substituted *s*-triazines are prepared by the reaction of urea with aliphatic or aromatic nitriles over a boron phosphate catalyst[131], and N-vinylamides are obtained in high yields by the catalytic dissociation of N(α-alkoxyalkyl) compounds in the presence of boron phosphate.[132]

It has also been reported that in a study of possible inhibitors of oxidative phosphorylation[133], boron phosphate inhibits phosphate esterification and, to a lesser extent, oxygen consumption.

CATALYTIC PROPERTIES

Moffat and co-workers[134–7] have studied the surface chemistry of boron phosphate in relation to its catalytic properties and claim that its catalytic activity is not explicable on the basis of the properties of phosphorus pentoxide and boric oxide. Samples of boron phosphate, each containing excess of phosphorus pentoxide, were pre-heated to various temperatures before use as catalysts for the decomposition of formic acid. Changes in catalyst weight during reaction and in the surface area after reaction were recorded. It was found that the surface area of boron phosphate increased during thermal treatment *in vacuo*, reaching a maximum value at 200°–300°C. After exposure to formic acid the surface area was found to have decreased in all cases.[137]

The specific surface of boron phosphate catalysts increases with the temperature of preparation up to a temperature of 200°C and then decreases.[7] The specific acidity per unit surface, determined with butylamine, showed a minimum when the catalyst was prepared at 600°C. The catalyst prepared at this temperature showed maximum activity with respect to the dehydration of amyl alcohol. Boron phosphate calcined up to temperatures of 400°C or 660°C showed maximum activity in the catalysis of the dehydration of pyrocatechol and methanol mixtures.[51] The catalytic activity of boron phosphate is also affected by its acidity, which may be brought into the desired range by exposing the catalyst to solutions of phosphoric, sulphuric, benzene sulphonic and arsenic acids.[5,138]

Gesmundo and Lorenzelli[139] have studied the infra-red spectrum of boron phosphate in the 2–150-μ region and propose correlations between its structure, as deduced from its spectrum, and its catalytic activity.

The patent literature gives details of the manufacture of boron phosphate catalysts in spherical form[140] and in granular form[9], the activation of boron phosphate isomerization catalysts by the addition of transition metal oxides which permit regeneration of the catalyst at lower temperatures[141], and the use of particles of boron phosphate in the 100–200-μ size range as catalysts for fluidized-bed reactions.[142]

Non-Catalytic Uses

CERAMICS AND GLASSES

The use of boron phosphate in ceramics and glasses has been proposed by a number of authors and many applications have been patented. Its principal use in ceramics is as a flux.[143] Its relatively high cost has, however, prevented any large-scale commercial exploitation in this field. Laboratory studies and proposed applications are surveyed below.

Translucent ware may be made from mixtures based on boron phosphate, pegmatite and kaolin with additions of various clays.[144] A translucent porcelain containing 25–50% by weight of boron phosphate has also been described.[145]

The firing temperature of hard porcelain may be decreased to 1200°–1250°C by addition of boron phosphate, and deformation of the ware made at these temperatures is reduced.[146–7] An addition of about 1·5% of boron phosphate gives the best results. Boron phosphate promotes the formation of mullite and cristobalite phases in porcelain based on quartz and cristobalite, although the effect depends upon the overall composition of the porcelain; it also exerts a fluxing effect which considerably reduces the fusion temperature.[148–50] The proportion of boron phosphate used in this work ranges from 0·5% to 2·0%.

Some physical effects of additions of boron phosphate to ceramic glazes have been described by Lehnhaeuser[151], while improved electrical properties and mechanical strength, together with resistance to thermal shock, are claimed for a composition based on wollastonite containing 2–10% of boron phosphate.[152] Dense, crystalline ceramic bodies composed of 38–45% boron phosphate with the remainder silica have electrical properties which compare favourably with those of fused silica and are usable at higher temperatures.[153] The dielectric properties, electrical resistivity and thermal expansion of boron phosphate–silica compositions, in both the glassy and devitrified states, have been measured by Kim and co-workers.[154–7] Boron phosphate has also been used to substitute silica in a mica-like crystal having a structure similar to that of fluorophlogopite.[158]

The structures of glasses prepared from boron phosphate and aluminium phosphate[159] and from boron phosphate, aluminium phosphate and silica[160] have been studied. Optical glasses containing boron phosphate have been patented[161–2], as have heat-absorbing glasses containing 2–8% of boron phosphate.[163–4] Other heat-absorbing glasses have also been described.[165] Water resistance of some alkali and alkaline–earth borophosphate glasses has been shown to be an order of magnitude superior to the corresponding simple phosphate glasses.[260] The use of borophosphate glasses for the fixation of radioactive wastes has been described[166], and the use of glasses made from vanadium pentoxide and boron phosphate as cathodes in voltaic cells has been patented.[167]

LUMINOPHORS

Boron phosphate activated with manganese gives a luminescence after irradiation with ultra-violet light at 365 mμ[168], whilst material activated with a thallium salt and irradiated at 254 mμ shows a maximum luminescence at 410 mμ. The preparation and properties of thallium-activated boron phosphate luminophors have been reviewed.[169] A cathodo- or photo-luminescent glass in which boron phosphate is used as a modifier has been patented.[170]

OTHER APPLICATIONS

Boron phosphate dispersed in phosphoric acid has been used as the electrolyte in intermediate-temperature fuel cells.[171] Such electrolytes are thermally stable, reject carbon dioxide, have high ionic conductivity and good mechanical properties. Sulphuric acid gelled with boron phosphate, in the ratio of 20–200 moles of H_2SO_4 to 1 mole of BPO_4, is used as the electrolyte in lead–acid accumulators.[172–4]

Patents have been granted for the use of: (a) boron phosphate esters as petrol additives to reduce engine deposits[22, 53]; (b) boron phosphate–amine adducts to suppress surface ignition[175]; and (c) boron phosphate in phosphate coating baths[176], as a stabilizer of chemoplastic polycarbonates[177–8], in the making of moulds for castings[179–80], and as a desiccant.[181] Other patents propose the use of boron phosphate formed *in situ* as an electrical insulator[182], as a component in the manufacture of electrical insulating tape[183], and in the encapsulation of semiconductors.[184] It has also been proposed to use solid solutions of metal oxides in a boron phosphate lattice as pigments and fillers.[60–61]

Boron phosphate can be applied as a source of boron for plant life by treating the plants with this material in a form that slowly releases soluble boron.[185]

Metal Borophosphates

Borophosphoric acid and complex borophosphates exist in solution, when the solution has sufficiently high concentration.[186–7] This conclusion was reached after a study of the solubility of boric acid in water and saturated potassium dihydrogen phosphate solution, and of the solubility of potassium dihydrogen phosphate in water and saturated boric acid solution. Further evidence was adduced from the volatility of boric acid in steam in the presence of inorganic and organic compounds. The existence of sodium borophosphate in solutions of boric oxide in fused sodium phosphate is indicated by the thermodynamic properties of these solutions.[188]

Copper and lead borophosphates having the general formula $MBPO_5$ have been prepared[189] by heating to dryness the appropriate metal oxide with syrupy phosphoric acid and boric acid in equimolar proportions; excess of boric acid was then added and the mixture fused at 1100°C to form two layers, the upper being excess of boric oxide and the lower the metal borophosphate. Cadmium borophosphate, $CdBPO_5$, has also been prepared by a similar process.[190]

The preparation of calcium, strontium and barium borophosphates of the same general formula by thermal synthesis has been reported.[191–2] *X*-ray powder diagrams show these compounds to be isostructural. The structure is of hexagonal form with 3 molecules per unit cell. These compounds, which melt incongruently, are stable in methanol but are decomposed by water and dissolved by dilute acids.[191] The compound $2CaO,P_2O_5,B_2O_3$ was prepared by heating $CaHPO_4,2H_2O$ and H_3BO_3 to 600°C, drying then heating in oxygen at 900°C for 3 days.

Compounds having the general formula M_3BPO_7, in which M is magnesium, manganese, cobalt, nickel, zinc or cadmium, have been made[192] by fusion of the appropriate oxides. Lead borophosphates having the compositions $PbBPO_5$, $Pb_4P_4B_2O_7$ and Pb_4BPO_8 exist in the system $PbO–P_2O_5–B_2O_3$.[193]

Borophosphoric acid, H_6BPO_7, has been patented[193] as a rust-inhibiting agent in steel pickling baths, as an absorbent for gases such as carbon dioxide, hydrogen sulphide and mercaptans[194], and as a component of oil additives.[195] Tetraborohypophosphoric acid, $B_4O_7(H_3P_2O_6)_2$, prepared by mixing phosphorus pentoxide and powdered boric acid with a little water, is a catalyst for the polymerization of olefins.[196]

Alkali-metal borophosphates have been proposed[197] as a constituent of coatings to provide a hardened surface for lightweight insulating panels, while mixtures containing sodium borophosphate provide heat-protective coatings in the manufacture of incandescent lamps.[198]

BORON ARSENATE

Preparation

Boron arsenate has been prepared from boric acid and arsenic acid by two techniques. Levi and Ghiron[23] heated equimolar proportions of concentrated arsenic acid solution and boric acid to dryness on a water bath and dried the product under vacuum to obtain pure boron arsenate:

$$H_3AsO_4 + H_3BO_3 \rightarrow BAsO_4 + 3H_2O$$

Schumb and Hartford[199] report the preparation of boron arsenate from aqueous solution. Arsenic acid dissolved in water is heated to boiling point and boric acid added. The solution is maintained at boiling point until a white precipitate is formed; this precipitate is washed by decantation, filtered and dried. The dried residue is finally boiled with ethanol to remove free boric acid.

Levi and Ghiron[23] also prepared boron arsenate by heating solid diammonium hydrogen arsenate with solid boric acid under reduced pressure:

$$(NH_4)_2HAsO_4 + H_3BO_3 \rightarrow BAsO_4 + 2NH_3 + 3H_2O$$

Kordes[200] studied glasses made from boric oxide and arsenious oxide, but no evidence of compound formation is reported.

Structure

Schulze[34–5] reports that boron arsenate has a low-cristobalite structure identical with that of boron phosphate. As in the latter case the boron and arsenic atoms are surrounded tetrahedrally by oxygen atoms, each oxygen atom belonging to two tetrahedra. The space-group of the structure is S_4^2–$\bar{I}^4$ and Schulze quotes the following crystal lattice constants: $a = 4{\cdot}459$, $c = 6{\cdot}796$ Å, both $\pm 0{\cdot}006$ Å, with 2 molecules per unit cell. Identical values for the crystal lattice constants have been reported by Levi and Ghiron.[23] Beekenkamp and Stevels[160] state that boron arsenate is isostructural with silicon dioxide in its crystalline state but not in its vitreous state. In vitreous boron arsenate the As^{5+} ions are surrounded by three bridging oxygen ions and one non-bridging oxygen ion.

High-density forms of boron arsenate prepared at high pressures have been studied by Dachille and co-workers[37–8] and by Mackenzie et al.[39] The crystal lattice constants for high-density boron arsenate are: $a = 4{\cdot}562$, $c = 10{\cdot}33$ Å, with 3 molecules per unit cell; the structure of this form is derived from that of quartz by doubling the *c*-axis. The crystal lattice constants for boron arsenate prepared at 1000°–1200°C at a pressure of 85,000 atm are $a = 7{\cdot}91$, $c = 10{\cdot}32$ Å, with 9 molecules per unit cell.

Physical Properties

The density of boron arsenate prepared at atmospheric pressure is reported by Schulze[35] to be 3·660 g cm^{-3} while Schumb and Hartford[199] give the value 3·40 g cm^{-3}. The densities of the forms prepared at high pressures are stated to be 4·00 g cm^{-3} [38] and 3·9 g cm^{-3}.[39]

Beekenkamp [159–60] states that boron arsenate melts at about 1100°C and forms a glass on cooling, while another investigation found that it does not melt at red heat but is slightly decomposed. Other workers[201] have found that when heated in air boron arsenate decomposes at 810° ± 5°C to form arsenious trioxide and boric oxide:

$$2BAsO_4 \rightarrow As_2O_3 + B_2O_3 + O_2$$

Schumb and Hartford[199] give a value of 1·66 for the refractive index of boron arsenate, while Schulze reports a figure of 15·54 for its molecular refraction. Schulze[202] has discussed possible reasons for the discrepancies in the reported values of the refractive index and density.

Beekenkamp[159] has reported the infra-red spectra of both the crystalline and vitreous forms of boron arsenate, while Bray and co-workers[30] have given n.m.r. data relating to this material.

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Chemical Properties

Boron arsenate is stated by Gruner[50] to form tri- and hexa-hydrates which do not form addition compounds with ammonia but which, on extraction with liquid ammonia, form $BAsO_4,3H_2O,NH_3$. This behaviour exactly parallels that which Gruner also found for boron phosphate, and he postulates that the trihydrate of boron arsenate is an acid of the same type as that proposed for boron phosphate trihydrate. Both the tri- and hexa-hydrates were found to decompose into the parent acids in aqueous solutions.

Anhydrous boron arsenate hydrolyzes in hot water to form boric and arsenic acids.[199,201] It is also reported that boron arsenate is decomposed by warm solutions of sodium carbonate or sodium hydroxide, and that it is soluble in both dilute and concentrated nitric acid. In concentrated hydrochloric acid boron arsenate reacts to form arsenious chloride and chlorine. Boron arsenate is soluble in dilute sulphuric acid but not in cold concentrated sulphuric acid[199]; it does, however, form gels in concentrated sulphuric acid.[54]

Boron arsenate may be reduced to the elements by ignition with aluminium or calcium silicide if a primer of potassium or sodium nitrite and calcium silicide is used.[63]

Metal Boroarsenates

Levi and Curti[187] reported results which indicate that boroarsenic acid exists in solution, even in the presence of energetic hydrolyzing agents, if the solutions are of sufficiently high concentration. Levi and co-workers[186] also state that complex potassium boroarsenates are formed in concentrated aqueous solutions of boric acid and potassium dihydrogen arsenate.

Bauer[191] describes the formation of calcium and strontium boroarsenates of the form $MBAsO_5$ by thermal synthesis. These compounds are stated to have a hexagonal structure containing 3 molecules per unit cell and to melt incongruently. A hydrated form of calcium boroarsenate, $Ca_2BAsO_4(OH)_4$, occurs as the mineral cahnite.[203] This compound forms tetragonal crystals with crystal lattice constants $a = 7{\cdot}11$, $c = 6{\cdot}20$ Å, and it has 2 molecules per unit cell. Its structure is similar to that of zircon but it is a derived structure based on KH_2AsO_4, so that the formula may be written $CaH_2B_{1/2}As_{1/2}O_4$.[204]

BORON–OXYGEN COMPOUNDS OF OTHER GROUP V ELEMENTS

Antimony

Antimony borate does not appear to have been described as such, although glasses may be made by fusing the parent oxides together. The equimolar B_2O_3–Sb_2O_3 glass is described as light lemon yellow in colour, but colourless if less than 31 mol-% of Sb_2O_3 is present.[284] Later research showed that clear glasses were obtained at up to 35 mol-% Sb_2O_3, with small particles of an undissolved phase present in melts of higher concentrations.[285] In neither study, nor in a later examination of the B_2O_3–Sb_2O_3 system[286], was a crystalline compound detected. B_2O_3–Sb_2O_3 glasses are slowly hydrolyzed in cold water.[201]

Bismuth

Levin and McDaniel[211] found four congruently melting compounds to exist in the Bi_2O_3–B_2O_3 system. These compounds, which may be considered as bismuth borates, are $2Bi_2O_3,B_2O_3$, $3Bi_2O_3,5B_2O_3$, $Bi_2O_3,3B_2O_3$ and $Bi_2O_3,4B_2O_3$. Their melting points are 675°C, 722°C, 708°C and 715°C, respectively. The last of these compounds shows a sluggish transformation at 696°C. The crystal structure of $2Bi_2O_3,B_2O_3$ has recently been determined[254] and the compound classified as an oxide–orthoborate, $Bi_4O_3(BO_3)_2$. It is monoclinic with the space-group $P2_1/c$ with the cell dimensions $a=11{\cdot}107$, $b=6{\cdot}627$, $c=11{\cdot}044$ Å and $\beta=91{\cdot}04°$. A body-centred cubic phase having the approximate composition $12Bi_2O_3,B_2O_3$, which melts incongruently at 632°C, was also identified. It was found in later work that the product of fusing bismuth oxide and boric acid contained two different phases, depending on cooling conditions, but both were polymorphs of $BiBO_3$.[253] At 600°C this compound decomposed to $2Bi_2O_3,B_2O_3$ and $3Bi_2O_3,5B_2O_3$. Hyman[254] described the 2:1 borate as an oxide–orthoborate and assigned the formula $Bi_4O_3(BO_3)_2$. The compound is monoclinic. Recently, sillenite phases have been found within the system Bi_2O_3–BPO_4 but not in Bi_2O_3–B_2O_3.[276–7]

Some electrical properties of bismuth borate glasses have been determined.[212] The dielectric constant ranges from 14·1 to 14·25 at 1 kHz and from 10·3 to 31·1 at 9600 MHz. The electrical resistivity of these glasses ranges from 0·0058 ohm cm to 340 ohm cm at 130°C and from 1·79 ohm cm to a value greater than 2·10 ohm cm at 230°C.

Vanadium

Boron vanadate, BVO_4, has been prepared by fusing together boric acid and vanadium pentoxide[160]:

$$2H_3BO_3+V_2O_5 \rightarrow 2BVO_4+3H_2O$$

The product melts at 600°–800°C[159–60] and remains glassy if quenched very rapidly from this temperature. The material devitrifies if cooled somewhat less rapidly after fusion.[160] The infra-red spectrum of vitreous boron vanadate shows that the V^{5+} ion is surrounded by three bridging oxygen ions and one non-bridging oxygen ion, and it also shows a band due to V–O vibration. Studies of boron vanadate prepared at high temperatures and pressures have not shown other structural forms to exist.[37]

A compound of the formula VBO_3 is prepared by heating the metal oxide and chloride with boric oxide in a sealed quartz tube.[205] This compound is stated to have a calcite structure. It is a ferromagnetic semiconductor.[263] Phase diagrams of the vanadium pentoxide–boric oxide system, and the vanadium pentoxide–borax system, have been published.[206–7] The former shows no eutectic, while the latter shows two eutectics and compound formation at three compositions. Another study of the vanadium pentoxide–boric oxide system demonstrated a weak interaction between these oxides.[208]

According to Ghiron, bivalent metals form borovanadates of two general forms: $2M^{II}O,3B_2O_3,V_2O_5$ and $M^{II}O,B_2O_3,V_2O_5$.[190, 209] These salts are prepared by maintaining fusions of the metal oxide, carbonate or hydroxide with vanadium pentoxide and excess of boric oxide at 1000°C for several hours. Lead and cadmium borovanadates of the first type, and lead, cadmium and zinc borovanadates of the second type have been prepared in this way. All these salts hydrolyze very readily and cannot be prepared in aqueous solution.[209]

The preparation of the compounds $4FeO,B_2O_3,V_2O_3$, $4CoO,B_2O_3,V_2O_3$ and $2MgO,B_2O_3,V_2O_3$ by electrolysis from molten baths at temperatures in the range 850°–900°C, as well as their crystallographic parameters, have been reported.[210]

Niobium

Passing reference is made by Fujiwara to the relative solubilities of nobium borates, phosphates and sulphates.[214]

Tantalum

Tantalum borate, $TaBO_4$, has been prepared[213] by fusing tantalum pentoxide and boric oxide in the proportion 1 to 15; crystalline tantalum borate separates from the melt. The lattice constants of the crystals, which are of the zirconium silicate type, are $a=6{\cdot}201$ and $c=5{\cdot}475$ kX, and the space group is $D_{4h}^{19}-I4/amd$. The interatomic distances are B–O(d) 1·43 kX, Ta–O(e) 2·03 kX and Ta–O(f) 2·10 kX. Blasse and Van den Heuvel[262] confirmed the zircon structure and commented upon the unusual coordination for the cations: Ta^{5+} in 8- and B^{3+} in 4-coordination. The infra-red and Raman spectra were measured. $TaBO_4$ showed a bluish-white luminescence under ultra-violet excitation at liquid-nitrogen temperatures.

The relative solubility of niobium and tantalum borates is mentioned by Fujiwara.[214]

BORON–OXYGEN COMPOUNDS OF GROUP VI ELEMENTS

Sulphur

Levi and Gilbert[15] reported the existence of two boratosulphates in the B_2O_3–SO_3–H_2O system at 25° and 45°C. These compounds were formulated as $H_3BO_3,B_2O_3,SO_3,4H_2O$, which forms fine, white crystals, and $3B_2O_3,SO_3,3H_2O$, which forms larger, colourless crystals. During a more recent study at 25°C, Nowdjavan et al.[259] isolated and characterized by *X*-ray diffraction the compounds: $SO_3,B_2O_3,4H_2O$; $SO_3,3B_2O_3,3H_2O$; $6SO_3,B_2O_3,8H_2O$; $6SO_3,2B_2O_3,4H_2O$; $6SO_3,B_2O_3,3H_2O$; $4SO_3,B_2O_3$ and $2SO_3,B_2O_3$.

Gillespie and co-workers[219] found that boric oxide and boric acid both give the ion $B(HSO_4)_4^-$ on solution in anhydrous sulphuric acid:

$$B_2O_3 + 9H_2SO_4 \rightarrow 2B(HSO_4)_4^- + 3H_3O^+ + HSO_4^-$$

$$H_3BO_3 + 6H_2SO_4 \rightarrow B(HSO_4)_4^- + 3H_3O^+ + 2HSO_4^-$$

In oleum, tetra(hydrogen sulphate) boric acid, $HB(HSO_4)_4$, which is a strong acid having a K_a value of 0·2[220], is formed. This acid was prepared by the reaction of boron trichloride with sulphuric acid[221]:

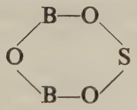
$$BCl_3 + 4H_2SO_4 \rightarrow HB(HSO_4)_4 + 3HCl$$

The formation of boron tri(hydrogen sulphate), $B(HSO_4)_3$, by the reaction of boron trichloride with anhydrous sulphuric acid, is also reported. Arotsky and Symons[222] found that boron trichloride reacts with oleum to give a non-conducting compound which was thought to be $B(HS_2O_7)_3$. This compound in turn reacts with $HS_2O_7^-$ ions to give $B(HS_2O_7)_4^-$ ions.

The cryoscopic behaviour of boric acid and boric oxide in disulphuric acid has been interpreted[223] in terms of the formation of a complex sulphato-boric acid, $HB(HS_2O_7)_4$, which appears to be a strong acid in disulphuric acid.

A study of the B_2O_3–SO_3 system showed only one compound, $B_2O_3,2SO_3$, to be formed.[224] It may be prepared by heating boric oxide with excess of sulphur trioxide in a sealed tube to a temperature greater than 150°C for 12 h. This compound is extremely hygroscopic but is stable in dry air. It decomposes at above 100°C.

Gillespie and co-workers[219, 225] obtained salts of tetra(hydrogen sulphate) boric acid by neutralizing sulphuric acid solutions of this acid with sulphuric acid solutions of the equivalent quantities of the normal sulphates of potassium, sodium, ammonium, barium and strontium, and of 2,4-dinitroaniline. They consider that these salts are best formulated as polysulphatoborates containing the ring:



and state that sulphatoborates previously described by other authors can also be formulated satisfactorily on this basis.

The existence of compounds having the formulae $Na_2S,2B_2O_3$, $Na_2S,3B_2O_3$ and $Na_2S,4B_2O_3$ in the glasses formed in the system Na_2S–B_2O_3 has been reported[226], while the compound $Al(SO_4)_3,B_2O_3$ is mentioned in a Russian patent.[227]

Selenium

Selenium borates do not appear to have been prepared.

Tellurium

Pavlova et al.[261] made a study of the TeO_2–B_2O_3 system by thermal analysis over the range 50–100 mol-% TeO_2. They found a region of two immiscible liquids extending from 50–95 mol-% TeO_2.

Chromium

Chromium borate, $CrBO_3$, is prepared by heating a mixture of chromium trioxide and calcium carbonate with a large excess of boric acid at 1100°C for 12 h.[215] It has also been prepared by heating chromium trioxide and chromium dichloride together with boric oxide and boric acid at about 1000°C in a sealed container.[205] Russian workers later prepared it by the careful dehydration and calcination of a mixture of boric and chromic acids.[266] Chromium borate forms rhombohedral crystals based on hexagonal cells, the lattice constants of which are $a = 4{\cdot}577$ and $c = 14{\cdot}25$ Å; they have a density of $4{\cdot}2\ \mathrm{g\,cm^{-3}}$.[215] It is isotypic with VBO_3 but, by contrast, $CrBO_3$ is antiferromagnetic.[263] Chromium borate decomposes at 1220°C into chromium trioxide and boric oxide.[215] Hydrated compounds of the general formula $2Cr_2O_3$,$3B_2O_3$,nH_2O ($n = 13$ or 18) have been prepared in dispersed form from aqueous solution.[267]

Complex bivalent chromium–boron compounds having the composition $CrXOH$,H_3BO_3 (X is chlorine, bromine or iodine) have been prepared[216] and are claimed to be usable in chromium-plating baths. They are made by mixing the chromium dihalide solution with boric acid, or boric acid and borax, or boric acid and calcium carbonate at pH 2·5–4·5 in the absence of air. The precipitate obtained consists of tetragonal crystals and is stable in air when dry.

Molybdenum

Schumb and Hartford reported that boric acid and molybdic acid did not enter into complex formation[217], and there are no reports of the existence of molybdenum borates. Russian workers confirmed this finding almost forty years later.[264] The shape of the solidus curve obtained in a study of the MoO_3–B_2O_3 suggested a metastable demixing into a crystalline phase (MoO_3) and a glassy phase (B_2O_3), but no binary solid phase. A similarly negative result was reported[218] for boromolybdates. However, Russian workers were later able to synthesize octahedral crystals of $3Na_2O$,B_2O_3,$24MoO_3$,$54H_2O$ by the anodic acidification of a sodium molybdate–boric acid mixture.[265]

Tungsten

12-Borotungstic acid is reported to exist in a number of hydrated forms. Kraus[228–30] has recorded compounds containing 14 and 31 molecules of water of crystallization, respectively, $H_5BW_{12}O_{40}$,$14H_2O$ and $H_5BW_{12}O_{40}$,$31H_2O$. The 14-hydrate is stated[229–30] to be triclinic and to be isomorphous with other complex tungstic acids. This compound is of the space-group C_i^1 and the unit cell contains 8 molecules. The 31-hydrate[228] is tetragonal and of the space-group D_{4h}^6, with 2 molecules per unit cell. In a later publication[231] Kraus and Mussgnug state that the only borotungstic acid is formulated as B_2O_3,$28WO_3$,$62H_2O$ (i.e., $H_5BW_{14}O_{46}$,$28\frac{1}{2}H_2O$), which does not accord with either the earlier work of Kraus or the later work of others.

Illingworth and Keggin[232] state that borotungstic acid is a pentahydrate and has a structure similar to that of phosphotungstic acid, $H_3PW_{12}O_{40}$,$5H_2O$. Signer and Gross[233] also found borotungstic acid to be a pentahydrate and thus to have the formula $H_5BW_{12}O_{40}$,$5H_2O$. Ripan and co-workers[234–9] have studied 12-borotungstic acid extensively and confirm[236] that the formula of this compound is $H_5BW_{12}O_{40}$. The constitutional formula for this acid in aqueous solution is $H_4H_5[B(W_2O_7)_6]$[234], which dissociates into $5H_3O^+$ and the complex anion $BW_{12}O_{40}^{5-}$ [235], and is pentabasic.[237]

Souchay[218, 240] states that two isomeric forms of 12-tungstoboric acid exist which differ only in the arrangement of the W_3O_{10} groups, and that 12-borotungstates are converted into 11-borotungstates at about pH 6, the reverse reaction occurring at pH values less than 4.

The absorption spectrum[241] of borotungstic acid in the ultra-violet region has been investigated, and Brown[242] has studied its thermal decomposition, together with that of its potassium salt and its ether-addition compound.

Borotungstic acid, recorded as $H_5BW_{12}O_{40},30H_2O$, improves the quality of chromium-plated surfaces when added to a conventional chromium-plating bath.[243] It has also been proposed[244] to use borotungstic acid in photosensitive systems.

A gaseous boron tungstate, BWO_4, was identified in the vapour over the WO_3–B_2O_3 system at 1520°K using effusion and mass spectrometric techniques.[268]

The following salts of borotungstic acid have been reported: ammonium[228, 245], sodium[246, 256], potassium[247], barium[246, 248], copper[248–9] and cobalt.[248]

Ammonium 12-borotungstate, $(NH_4)_5BW_{12}O_{40},26H_2O$, is tetragonal[228] with 2 molecules per unit cell, and is isomorphous with the 31-hydrate of 12-borotungstic acid. The infra-red spectrum of this compound has been recorded.[245]

Sodium borotungstate, $Na_5BW_{12}O_{40},2H_2O$, has been prepared[246] from stoichiometric proportions of boric acid and sodium tungstate. It was later recognized that there are various forms of sodium borotungstate, obtainable by anodic acidification of sodium paratungstate–boric acid mixtures.[269] The Na_2O,B_2O_3–Na_2O,WO_3–WO_3–B_2O_3 anhydrous (glassy) system has been studied.[270]

Potassium borotungstate, $K_5BW_{12}O_{40},18H_2O$, is prepared by addition of potassium carbonate solution to a nearly saturated solution of borotungstic acid[250]; this compound also exists in forms containing 12 and 5 molecules of water of crystallization. A hydrated salt with 2 molecules of water of crystallization was not observed.[250] The phase diagram of the anhydrous system B_2O_3–WO_3–K_2O shows the formation of one compound, $3K_2O,3B_2O_3,4WO_3$ (congruently melting) and three eutectics.[271]

Barium borotungstate, $Ba_5H_8[B(W_2O_7)_6]_2$, is made in 55% yield by treating sodium borotungstate with barium carbonate.[246]

The copper borotungstate–water system has been studied[249] over the temperature range 0°–70°C. The existence of five crystalline hydrates containing 57, 63, 69, 74 and 77 molecules of water of crystallization was established.

Borotungstic acid and borotungstates are claimed to catalyze ester-interchange between glycols and esters of dicarboxylic acids in reactions leading to the formation of linear polyesters.[251]

The existence of a complex borovanadotungstic acid, $H_5BW_{10}V_2O_{39},21H_2O$, has been recorded.[252]

Uranium and Americium

Hexavalent uranium is reported to react with molten boric oxide at 900–1100°C to give UO_3,B_2O_3 (or $UO_2(BO_2)_2$).[274] It is thermally stable up to 1100°C in air in the presence of excess boric oxide, but decomposes at 750°C if boric oxide is absent. The crystals are greenish-yellow and are insoluble in water, but hydrolyze slowly. Alkali uranyl borates having the formula $M_2O,2UO_3,B_2O_3$ (or MUO_2BO_3) are also known.[274] U_3O_8 was reported to have a solubility in boric oxide of 3·2% at 1200°C.[283] There is no evidence for the existence of hydrated uranium borates.

Americium borate, Am_2O_3,B_2O_3, has been reported.[275] It has properties similar to the corresponding lanthanide borates and has an aragonite structure. Lattice constants have been determined.

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SECTION A14

PERBORATES

BY C. A. MORGAN

INTRODUCTION

Inorganic peroxides and soluble borate salts readily react to form solid compounds containing usually one atom of active oxygen and one univalent cation per boron atom. They are commonly known as *perborates*, although they are more strictly termed *peroxyborates*. Sodium perborate has received by far the greatest attention, doubtless because of the very large tonnages produced industrially.

Much interest has been shown in establishing the existence and nature of the perborate anion in solution and in the solid phase. Uncertainty arose from the facts (i) that perboric acid has never been isolated, and (ii) that perborates in solution show the reactions of hydrogen peroxide. Also, as solid perborates are exceptionally difficult, if not impossible, to obtain free from hydroxyl groups, there were doubts whether they are hydrated peroxyborates or borates with hydrogen peroxide of crystallization. Thus 'sodium perborate monohydrate' has been considered by some to have the structure $NaBO_3,H_2O$ and by others to be $NaBO_2,H_2O_2$. In 1961, it was conclusively shown that the anion, in the solid phase, is $[(HO)_2B(O_2)_2B(OH)_2]^{2-}$ and the above compound is therefore the anhydrous sodium salt of this anion.

For simplicity and to avoid confusion, the current widely-used terminology has been used throughout the following account, with the degree of hydration written as if the perborate anion were BO_3^-.

SOLUTIONS OF BORATES AND PEROXIDES

The formation of complexes between hydrogen peroxide and borates in solution has been studied over many years. In 1900 Constam and Bennett's[1] conductivity measurements suggested the formation of a monobasic acid. Pissarjewsky[2], in 1902, measured the distribution coefficient of hydrogen peroxide between ethereal and aqueous solutions of alkali borates; his results indicated that complexes in substantial amounts were formed, particularly at low temperatures.

An extensive series of investigations was carried out by Menzel and co-workers in the 1920s. They found[3-4] that the solubility of boric acid in aqueous hydrogen peroxide was slightly lowered as the concentration of the peroxide was increased, indicating negligible compound formation. Measurements of freezing-point depression, conductivity and distribution between solvents supported the conclusion that appreciable combination occurred only with borate anions and not with unionized boric acid. Complexes containing one molecule of borate and peroxide predominated in dilute solution (0·02 to 0·07 M), but at higher concentrations (as in solutions of borates alone), anions of higher molecular weight and charge tended to be formed.[13] For the 1:1 complex the decomposition constant was calculated to be

$$\frac{[BO_2^-][H_2O_2]}{[BO_2,H_2O_2^-]} = 0{\cdot}033 \text{ at } 18^\circ\text{C and } 0{\cdot}024 \text{ at } 0^\circ\text{C},$$

and the apparent dissociation constant

$$\frac{[H^+][BO_2,H_2O_2^-]}{[HBO_2][H_2O_2]} = 1{\cdot}7\times10^{-8} \text{ at } 18^\circ\text{C and } 1\times10^{-8} \text{ at } 0^\circ\text{C}$$

Since the 1950s the problem has been attacked by using newer physical methods with results which—apart from a variety of nomenclatures generally supporting the existence of more highly hydrated ions—generally agree with the earlier work. Measurements by Edwards[5] of the fall in pH of dilute aqueous solutions of boric acid on addition of hydrogen peroxide gave some evidence pointing to the formation of several more complex species of the type $[B(OH)_{4-n}(OOH)_n]^-$, although that with $n=1$ appeared to predominate. The stability of the perborate anion in alkaline solution and its effect on pH are illustrated by Edward's conclusion that, at 25°C, in a solution initially 0·05 M in $Na_2B_4O_7$ and 0·04 M in H_2O_2 (pH 9·0), 29% of the borate is combined as a perborate; the proportion increases to 97·6% in 0·8 M H_2O_2 (pH 7·5).

Equilibrium constants in general agreement with those found earlier were obtained by Kern[6] by polarography; he found that the constant for the equilibrium, which he expressed as

$$\frac{[H_2O_2][B(OH_4)^-]}{[H_2O_2,B(OH)_4^-]}$$

rose from 0·03 to 0·05 moles/l as the borate concentration was decreased from 0·2 M to 0·03 M.

Antikainen[7], using a differential potentiometric method, deduced the existence of two peracids, H_3BO_3,H_2O_2 and the corresponding dimer, with complex formation constants of $1{\cdot}2\times10^{-8}$ and 2×10^{-8}, respectively, at 25°C for the two reactions:

$$H_3BO_3+H_2O_2 \rightleftarrows H^+ +(H_2BO_3,H_2O_2)^-$$

and

$$2H_3BO_3+2H_2O_2 \rightleftarrows H^+ +(H_2BO_3,H_3BO_3,2H_2O_2)^-$$

For the reaction between the univalent borate anion and hydrogen peroxide to form the postulated anions $(H_2BO_3,H_2O_2)^-$ and $(H_2BO_3,2H_2O_2)^-$ he calculated values

$$\frac{[H_2BO_3,H_2O_2^-]}{[H_2BO_3^-][H_2O_2]} = 21{\cdot}1 \quad \text{and} \quad \frac{[H_2BO_3,2H_2O_2^-]}{[H_2BO_3^-][H_2O_2]^2} = 33{\cdot}6$$

The nature of the complex anion was considered by Wilson[8], who adduced evidence for preferring $HOOB(OH)_3^-$ to the alternative $H_2O_2,B(OH)_4^-$ on the grounds that nucleophilic substitution in boric acid of –OH by –OOH according to reaction (1) below was more probable than reaction (2) involving borate ion.

$$(1) \qquad B(OH)_3+H_2O_2+H_2O \rightleftarrows HOOB(OH)_3^- +H_3O^+$$
$$(2) \qquad B(OH)_4^- +H_2O_2 \rightleftarrows H_2O_2,B(OH)_4^-$$

This view of the mechanism was supported by the contrasting influence of borate in accelerating reactions, such as the oxidation of thiocyanates, in which hydrogen peroxide acts as an electrophile, but has no such effect on those reactions (e.g., with benzonitrile) in which hydrogen peroxide functions as a nucleophile. It also does not imply boron with the unusual coordination number of five.

In 1970 Koberstein et al.[9] reported cryoscopic measurements consistent with the predominance of the ion $[(HO)_2B(O_2)_2B(OH)_2]^{2-}$ in concentrated solutions, but with occurrence of dissociation on dilution to give univalent anions containing one boron atom.

Various authors have commented on the speed with which equilibrium is attained between the peroxyborate anion and hydrogen peroxide, and it has been shown polarographically that decomposition occurs via hydrogen peroxide[6], thus explaining why perborate shows the same chemical reactions as hydrogen peroxide.

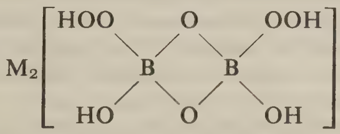
In aqueous solution the peroxidic oxygen atoms do not exchange with water, in contrast to the (non-peroxidic) oxygen atoms in borates; this was shown both by Franchuk and Brodski[45], who measured the ^{18}O content of oxygen evolved during the thermal decomposition of sodium perborate dissolved in $H_2{}^{18}O$, and by Edwards et al.[28], who found the same ratios of ^{18}O in dissolved $NaBO_3,4H_2O$ as in the hydrogen peroxide from which it had been made.

STRUCTURE OF SOLID PERBORATES

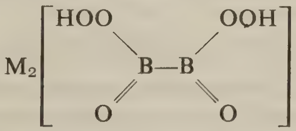
Much of the past disagreement about the existence of the perborate anion in the solid phase seems to have stemmed from the observations of Riesenfeld and Reinhold[10] and of LeBlanc and Zellermann[11], who claimed a distinction between true perborates with a peroxyborate anion, pseudo-perborates with firmly bound hydrogen peroxide, and those which were addition compounds containing hydrogen peroxide of crystallization. They based their views on the differing reactions of solutions with cold potassium iodide solution, with which it was claimed that the true perborates released iodine, the pseudo-salts did not react, and the addition compounds gave oxygen. For example, $NaBO_3,4H_2O$ was described as a pseudo-salt and $KBO_3,0{\cdot}5H_2O$ a true perborate. Although Menzel et al. at first supported this view[12], they later[13] queried it, having found that both reactions could occur simultaneously. But some other authors maintained that the peroxyanion did not exist, e.g.[15–16] The rapid equilibration in solution was apparently not realized at the time.

Evidence for peroxyborate anions was also adduced from the existence of solid perborates containing larger amounts of active oxygen than could be ascribed to peroxide of crystallization, e.g., Partington and Fathallah[17–18] prepared $LiBO_4,H_2O$, $NaBO_5,H_2O$, $RbBO_4,0{\cdot}5H_2O$ and $CsBO_4,0{\cdot}5H_2O$. Other workers also showed interest in dehydrating ordinary perborates with one active oxygen atom per boron atom. The problem was, however, not satisfactorily explained until use was made of newer non-destructive physical methods.

Prior to the introduction of most of the modern methods for examining solids Menzel[13], in 1927, deduced from cryoscopic measurements on concentrated solutions that perborates of general formula MBO_3,H_2O (e.g., $NaBO_3,H_2O$) should be represented as

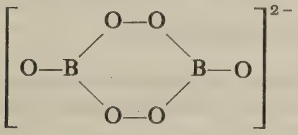


(containing boron with a coordination number of 4) and those of formula MBO_3,-$0{\cdot}5H_2O$ (e.g., with $M = K$ and NH_4) as

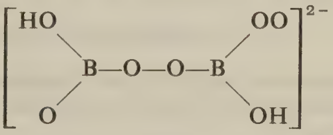


(with 3-coordinate boron) (see also [14]).

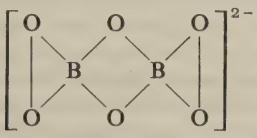
Other authors put forward structures such as **I** and **II** below for the 'pseudo' and 'true' per-salts (Matejka[19]); **III** is due to Kretzschmar.[20]



I



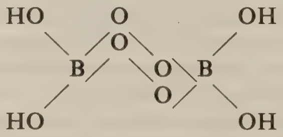
II



III

Theoretical arguments against structures with 4-coordinate boron were put forward by Carpeni.[21–2] Partington and Fathallah[18] favoured structures based on Menzel's views for the higher perborates.

In 1958 Connor and Richards[23] examined the proton resonance spectra of the crystalline perborates of sodium, potassium and rubidium and concluded that, as most of the hydrogen was present in water of crystallization, the salts contained mainly peroxy-anion with only small amounts of peroxide of crystallization. (This contrasts with their views on perpyrophosphates and percarbonates.) The tetrahedral configuration of boron was shown by NMR spectra of single crystals of $NaBO_3,4H_2O$ (Edwards et al.[24–5]). Conclusive evidence was given for the structure of the anion in 1961 by Hansson's *X*-ray crystallographic studies[26] on both single crystals and powders of sodium perborate prepared by methods previously claimed to have given specifically either $NaBO_3,4H_2O$ or $NaBO_2,H_2O_2,3H_2O$. Both methods gave a product with the structure:



i.e., with an anionic formula $Na_2[(HO)_2B(O_2)_2B(OH)_2],6H_2O$. From the similarities of several types of spectra, Koberstein and coworkers[9] recently concluded that $NaBO_3,3H_2O$ and $NaBO_3,H_2O$ were based on the same anion as $NaBO_3,4H_2O$.

Other work by several investigators supports the existence of a peroxyborate anion with a structure such as that above. Van Gelder[27] was unable to detect any partial pressure of water above $NaBO_3,H_2O$. Edwards et al.[28] showed that, whereas dehydration down to $NaBO_3,H_2O$ does not break peroxidic bonds, attempts to remove more water disrupt the molecule. The resultant product (see 'anhydrous sodium perborate' below) is a highly paramagnetic heterogeneous material containing O_2^- and O_3^- as well as peroxyborate radicals and possibly interstitial oxygen, shown by isotopic studies to have originated entirely from peroxidic groupings.

Unfortunately, there appears to have been no similarly extensive examination of the structures of $KBO_3,0{\cdot}5H_2O$, of anhydrous ammonium perborate, or of the anhydrous highly peroxidized sodium perborate mentioned subsequently.

SODIUM PERBORATES

Other perborates have not received nearly as much attention as sodium perborate tetrahydrate ($NaBO_3,4H_2O$) and the monohydrate derived from it. Several hundred thousand tons of tetrahydrate are produced annually. The only other well-characterized sodium perborate is the trihydrate, which was discovered relatively recently. Concern with other perborates, including so-called 'anhydrous sodium perborate', has largely stemmed from interest in the structure of the peroxyborate anion.

Sodium Perborate Tetrahydrate, $NaBO_3,4H_2O$

The preparation of sodium perborate tetrahydrate by both chemical and direct electrolytic methods has been studied extensively for both large- and small-scale production.

In the chemical methods the desired ratios of sodium, borate and peroxide are obtained by the appropriate choice amongst the possible reactants borax ($Na_2B_4O_7$,-$10H_2O$), sodium metaborate ($NaBO_2,H_2O$), boric acid, sodium peroxide and hydrogen peroxide, plus either sodium hydroxide or an acid. Early work is reviewed in Mellor, V, 115–21, and updated in Machu's book[29] on peroxidic compounds. German manufacturing processes current during the early 1940s have also been reported in detail.[30] There are also many patents describing process variations, but few recent papers.[31–2]

Industrially, the three most important routes have been:

1. the Castner–Kellner 'acid' process introduced in about 1915,
   $Na_2B_4O_7{,}10H_2O + 4Na_2O_2 + HCl + H_2O \rightarrow 4NaBO_3{,}4H_2O + 6NaCl$;
2. the 'duplex' process developed in the early 1920s,
   $Na_2B_4O_7{,}10H_2O + 4Na_2O_2 + 3H_2O_2 + 6H_2O \rightarrow 4NaBO_3{,}4H_2O + 6NaCl$;
3. that now most commonly used,
   (a) $Na_2B_4O_7{,}5H_2O + 2NaOH \rightarrow 4NaBO_2 + 6H_2O$,
   (b) $NaBO_2 + H_2O_2 + 3H_2O \rightarrow NaBO_3{,}4H_2O$.

The change in favoured reactants can be ascribed to progress in the manufacture of hydrogen peroxide. In method 3 borax (or a commercial tetraborate of lower hydration) and sodium hydroxide are dissolved in hot aqueous mother liquor to give a solution containing 200–600 g/l of sodium metaborate (in practice usually with a Na:B ratio slightly less than 1:1). This liquor is cooled to just above 0°C and mixed with cooled hydrogen peroxide in an agitated vessel fitted with equipment for refrigerative cooling. Sodium perborate tetrahydrate crystallizes out; it is separated from the recycled mother liquor and dried at restricted temperatures. Patents indicate that the reaction can take place in the presence of organic substances resulting from the manufacture of hydrogen peroxide by oxidation of isopropanol or by an anthraquinone process.

Considerable industrial attention has been paid to obtaining operating conditions which yield a product having a high resistance to decomposition during storage and having particles with size, shape, density and properties which resist caking and attrition, to suit blending with other components of detergent powders. Addition of substances such as magnesium salts, silicates, polyphosphates, detergents and stabilizers such as those used for hydrogen peroxide is also mentioned in the extensive patent literature.

As described in Mellor, V, 116, Tanatar in 1898 prepared sodium perborate by electrolysis of a solution of sodium borate alone, although his results were subsequently disputed.

Later workers have generally used methods based on the conditions evolved by Arndt and co-workers[33–4] who electrolyzed concentrated solutions of sodium carbonate (120 g/l) and borax (30 g/l). It appears to be accepted that temperatures of 10°–15°C, current densities of 10–20 A/dm^2 and concentrated solutions are beneficial. Additives such as chromate, silicate, fluoride, etc., have been recommended. For the anode, platinum is considered best and graphite tolerable, but anodes made of iron, bismuth, tungsten, molybdenum, copper or tantalum are not satisfactory. As cathodes tin, silver, copper and nickel are possible but seem inferior to platinum.[36–41] Current efficiencies up to 70–80% have been reported by Stepanov.[35] According to Khomutov and Sklyarov, replacement of sodium carbonate by the more soluble potassium carbonate improved the current efficiency to 93% at a current density of 50 A/dm^2.[43] Superimposition of alternating current was found to have no effect.[42]

The presence of carbonate ions appears essential[44–5], e.g., Matsuda[44] found that the yield of perborate was negligible if sodium hydroxide replaced the carbonate.

The anodic processes have been the subject of some investigation.[46–8] Hydrogen peroxide is not an intermediate, as Haïssinsky and Cottin found it to inhibit the formation of perborates and percarbonates.[46] The hypothesis that the first step in the reaction involves formation of percarbonate (presumably a perdicarbonate) was supported by Franchuk and Brodski[45], who carried out electrolyses using $H_2{}^{18}O$ and $Na_2C^{18}O_3$ with results which indicated that the percarbonate initially formed hydrolyzes to hydrogen peroxide, which then combines with the borate.

Electrolysis is believed to be no longer used industrially in the manufacture of perborate.

Sodium Perborate Monohydrate, $NaBO_3,H_2O$

Sodium perborate monohydrate can be obtained from the tetrahydrate by drying it over sulphuric acid or phosphorus pentoxide at room temperature, by washing with alcohol or by heating to 50°–55°C, either in a vacuum or, industrially, in a large flow of air, so that the temperature does not exceed 60°C and melting and decomposition are avoided.[15, 49–51] The reaction is reversible but, as discussed above, attempts to obtain further dehydration cause breakdown. Monohydrate has also been prepared by dehydration of the trihydrate. It is stated by Koberstein et al.[9] to have a density, solubility and vapour pressure which differ slightly from those of the product from the tetrahydrate.

Sodium Perborate Trihydrate, $NaBO_3,3H_2O$

In 1956, Van Gelder described a new hydrate ($NaBO_3,3H_2O$) which he made from the solid tetrahydrate either by keeping it in an enclosed space at 50°C for a considerable time or by heating an aqueous slurry of tetrahydrate for 4 hours at 50°C and thereafter drying the crystals at 40°C.[27, 52–3] Alternatively, solid or molten tetrahydrate can be heated to 70°C in the presence of a little mono- and tri-hydrate.[54]

The trihydrate can also be prepared from a solution of sodium metaborate and hydrogen peroxide by seeding the solution with crystals of the trihydrate.[55–6] Some workers advised that electrolytes which lower the solubility of the trihydrate should be absent[57] but others advocated their presence.[58] An alternative route is by reacting a solution of borate, excess alkali and hydrogen peroxide at 20° to 60°C and then treating with acid.[59]

Between 18° and 50°C the trihydrate is more stable than the tetrahydrate in contact with water, although it crystallizes more slowly. But below 15°C it is spontaneously converted into the tetrahydrate.

The thermal stability on storage at elevated temperatures, which is stated to be greater than that of the tetrahydrate, is claimed to be improved by the presence of magnesium silicate.[60]

Bulk supplies of the trihydrate seem not to be currently on the market.

Other Sodium Perborates

A compound $NaBO_2,NaBO_3,4H_2O$ was prepared by Van Gelder by heating $NaBO_3,4H_2O$ with excess sodium metaborate at 50°C and reacting the resultant crystals with hydrogen peroxide at 60°C. The product was stable only above 23°C, had a distinctive *X*-ray pattern, did not lose water at 80°C and melted at 88°C.[52]

An acid perborate with a formula corresponding to $NaH(BO_2,H_2O_2)_2$ was claimed to be formed by treating borax (1 mole) with 3 to 5 moles of hydrogen peroxide and evaporating at below 60°C under reduced pressure.[61]

So-called 'higher perborates' with more than one atom of active oxygen per boron have been obtained by Partington and Fathallah[17–18], who reacted solid sodium metaborate with excess hydrogen peroxide and then, with alcohol, precipitated products having analyses corresponding to formulae varying between $NaBO_{3\cdot85},1\cdot47H_2O$ and $NaBO_{4\cdot88},1\cdot02H_2O$. Kazragis and Prokopcikas[62] described an easier way of making these higher perborates from borates with higher boron to sodium ratios and large excesses of hydrogen peroxide. In this way $NaBO_{3\cdot6},1\cdot5H_2O$ was obtained, which could be almost completely dehydrated over desiccating agents. Alkali perborates of this type have poorly defined crystals, decompose explosively on heating and have solubilities in cold water of less than 100 p.p.m. Their low solubilities in all solvents have prevented measurement of their molecular weights, and apparently no detailed study of their structures has been carried out.

The patent literature also includes accounts of perborate compounds of unspecified composition, usually made by rapid drying of the reactants. They generally contain 16–20% of active oxygen, have Na:B ratios greater or less than unity and can contain ratios of water to active oxygen of less than 1:1. Some are said to have higher solubilities and stabilities than the common tetrahydrate (e.g., [63–6]).

Anhydrous Effervescent Sodium Perborate

Whereas sodium perborate tetra- and tri-hydrates can be reversibly dehydrated to the monohydrate, disruption of the molecules occurs in attempts to obtain further dehydration by heating (e.g., [68]). This is not surprising because the monohydrate has been observed to have a negligible partial pressure of water above it[52] and this fact is in agreement with modern views of the structure (see above).

By careful heating at 100°–130°C, products are formed which release oxygen on contact with water.[12–13, 15, 69] This reaction, observed only with perborates, was extensively studied by Edwards and co-workers[28, 70], who used a variety of physical and chemical techniques to examine what they called 'effervescent magnetic peroxyborates'. Their conclusions were that the materials were heterogeneous and contained O_2^- and O_3^- ions as well as a peroxyborate radical and possibly interstitial oxygen molecules.

Physical Properties of Established Sodium Perborates

Melting points of the established hydrates of sodium perborate are: $NaBO_3,4H_2O$, 65·5°C[52], 63°C[62]; $NaBO_3,3H_2O$, 82°C[52]; $NaBO_3,H_2O$, 70°C.[51] Only the tetrahydrate is hygroscopic.

The solubilities in water have been reported both by early workers and more recently[49, 51–2]; values lie between 1·5 and 4% at temperatures between 15° and 30°C. The trihydrate is less soluble than the tetrahydrate between 18° and 50°C.[27] Sodium metaborate decreases the solubility when present in amounts up to about 25 g/l but higher concentrations thereafter raise it.[71, 27] The solubility is increased by boric, tartaric and citric acids, glycerol, or small amounts of magnesium and ammonium sulphates. Alkali polyphosphates are stated to render the perborate freely soluble.[72]

The pressure of water over the tetrahydrate was found by Taylor and Taylor[49] to follow the equation

$$\log p = 12{\cdot}19 - 3{,}236/T$$

No detectable pressure of water vapour was found above the monohydrate.[27]

The standard heats of formation (25°C) of crystalline tetrahydrate and in (hypothetical) 1 molar solution are $-504{\cdot}8$ and $-220{\cdot}0$ kcal/mole[73]; these values are derived from results obtained by Tanatar in 1898.

The results of infra-red, NMR and ESR studies are given by Edwards et al.[28]; Connor and Richards[23]; Miller et al.[74]; Onak et al.[75]; and Koberstein et al.[9]

The piezoelectric properties were reported by Koptsik et al.[76]

Lattice constants for the tetra- and tri-hydrates have been determined by Van Gelder[52] and by Hansson.[26]

CHEMICAL PROPERTIES OF PERBORATES

Thermal Decomposition

On heating, sodium perborate ultimately decomposes into oxygen and sodium metaborate ($NaBO_2$). At about 250°C the reaction is rapid and complete, but on heating solid sodium perborate at 110°–130°C the anion is disrupted to give heterogeneous paramagnetic materials containing, inter alia, O_2^- and O_3^- (*v. supra*). On storage alone at room temperature, commercial sodium perborate tetrahydrate loses about 1% of active oxygen per year, but in detergent mixtures the rate is about 15 times as great.[77] Stabilizers are commonly incorporated in industrial products.

At its melting point, $NaBO_3,4H_2O$ dissolves in its water of crystallization with a consequent increase in decomposition rate. The mono- and tri-hydrates, with higher melting points, have lower rates of decomposition on warm storage.[27]

Thermogravimetric studies on perborates with one active oxygen per boron have been described by Koberstein[9]; Kazragis et al.[62] similarly examined the decomposition of perborates richer in oxygen. The thermal decomposition of sodium perborate in aqueous solution is of importance in view of its widespread use as a bleach. However, in such practical circumstances, conditions differ from those of a pure substance in simple aqueous solutions because of the presence of stabilizers, other constituents of detergents and the fabric being treated.

Sborgi and Nocentini, in 1920, found[78] the decomposition of a commercial sodium perborate in water to be approximately monomolecular, with a rate at 10°C about half that at 20°C; at 40°C it was found to be five to six times that at 20°C. Both boric acid and sodium hydroxide were observed to retard the reaction, whereas sodium metaborate slightly increased it. This observation conflicts with that of Jinkins and McGraghan[79], who found that the rate of decomposition increased with pH. The latter are supported by manufacturers' literature, which also indicates that a 1% solution decomposes in water to the extent of 15, 25 and 90% after five hours at 60°, 80° and 100°C, respectively. Lewis and Eggertsen[80] found that a solution containing equivalent quantities of boric acid, hydrogen peroxide and sodium hydroxide decomposed more rapidly than a solution of sodium perborate of the same concentration.

According to Sborgi and Nocentini[78], solid iron, nickel or zinc retards the decomposition, which they found is heterogeneously catalyzed only by metallic platinum, gold and copper. The dissolved ions of iron, copper, lead, mercury, cobalt and especially manganese accelerate decomposition, whereas tin, zinc, nickel and particularly cadmium ions decrease the rate. Hagen and Larsen obtained somewhat similar results at 100°C in distilled water.[81] Sodium silicate was stated by Dalström not to stabilize perborate dissolved in distilled water[82] but silica gel was claimed to be effective[83]; phosphate ions also acted as stabilizers.[84] Prokopcikas et al.[85] found the order of reaction to lie between 0 and 1 in the presence of nickel, cobalt or copper ions, which these authors considered to form unstable peroxides with cobalt and copper or unstable nickel perborates. The effect of inorganic ions under practical conditions and in the presence of polyphosphate was described by Heymer and Harnisch.[86]

Organic materials described as retarding decomposition of perborate in solution (as opposed to stabilizing the solid) include proteins[87], soap[78] and certain polyhydroxy compounds—such as gluconates and mannitol—which form complexes with borate ions.[88] Sborgi and Nocentini[78], found that certain compounds—e.g., tannic acid and acetanilide—which retarded the decomposition of hydrogen peroxide had far less effect on sodium perborate. Quantitatively, the effects of catalysts and stabilizers on the rates of decomposition outweigh the influence of pH and perborate concentration.

Considerable industrial attention has been given to activators, i.e., materials introduced with the aim of increasing the rate of bleaching at about 50° to 60°C. According to recent reviews by Gilbert[89], those usually favoured are either certain metals complexed with moderately strong agents or organic substances which form peracids, e.g., tetra-acetyl ethylene diamine and triacetyl cyanurate. The patent literature mentions, *inter alia*, copper salts[98], acyl esters of phosphonic or phosphinic acids[91], organic nitriles[92], chloracetyl salicylic acid[93], *p*-acetoxy benzene sulphonate[94], phthalic anhydride and formamide.[95]

The mechanisms of bleaching and thermal decomposition in solution are believed to follow those of hydrogen peroxide, where evidence points to the formation of a transition complex which either gives off oxygen or oxidizes a substrate.[77]

Other Chemical Reactions

As is to be expected from the rapidity with which hydrolysis occurs in aqueous solution and the similarity of polarograms to those of hydrogen peroxide, the chemical properties of solutions of sodium perborate in the main resemble those of the corresponding dilute solution of hydrogen peroxide and sodium borate. Rates of reaction may, however, be affected by the peroxyborate ion.[8, 86]

Early workers found, as described *inter alia* in Mellor, V, p. 118, that with sodium perborate concentrated sulphuric acid reacted to give ozonized oxygen; chlorine was released from hydrochloric acid; oxygen was evolved with bromine water, iodine, and quantitatively with sodium hypochlorite[97]; mercury and gold[98] were released from certain of their salts; ferrous ions were oxidized to ferric; and permanganate yielded manganese dioxide and oxygen. Chromates and titanic salts formed coloured substances (this last reaction forming[99] the basis of a test sensitive to 50 p.p.m. of hydrogen peroxide) as do the complexes of cobalt and iron with nitrilotriacetic acid[100] and manganese–picolinate complexes.[101]

More recently, workers have studied the reactions with sodium chlorate; in acid solutions, chlorine dioxide is formed at 60°C[102], whereas at lower temperatures perborate gives good yields of sodium chlorite, $NaClO_2$.[103–4] With sulphur dioxide, solutions of perborates give sulphate; hydrogen sulphide reacts to form mixtures of sulphate, sulphite, thiosulphate and dithionate.[105] Reactions with organic compounds include cleavage of α-diketones.[106] Oxidation of polyhydroxy-alcohols[107], e.g., glycerol, yields formaldehyde.[108] Perborate is also used for the oxidation of benzoic acid[109], as well as the industrially practised oxidation of vat and sulphur dyes and the bleaching of unwanted colorations, described below.

PERBORATES OF METALS OTHER THAN SODIUM

Lithium Perborates

$LiBO_3,2H_2O$ was made by Menzel and co-workers[12–13] by addition of alcohol to an aqueous solution of the borate and hydrogen peroxide. The monohydrate was prepared from it either by dehydration or on crystallizing a saturated aqueous solution at room temperature; its solubility is about 0·23 moles/litre at 18°C. On heating to 117°C abrupt loss of oxygen occurs, all active oxygen being lost on reaching 250°C.

Somewhat earlier, Bezner-Löwy[110] prepared a compound analyzing as $Li_2B_2O_5$,$2{\cdot}5H_2O$, both by chemical methods and by electrolysis of lithium borate plus potassium carbonate. The product was stable up to 50°C and showed the unusually high solubility of 10 g/100 ml water at room temperature.

Substances containing higher amounts of active oxygen were described by Partington and Fathallah[17–18], with formulae ranging from $LiBO_{2{\cdot}5},1{\cdot}5H_2O$ to $LiBO_{3{\cdot}93},1{\cdot}04H_2O$.

Potassium Perborates

Whereas the chemical and electrolytic[111] methods for preparing potassium perborates and their properties generally resemble those of the corresponding sodium salts, lower hydrates, e.g., KBO_3, $0{\cdot}5H_2O$, are more readily obtained.[12–13] For this hydrate, a dimeric anion containing 3-co-ordinate boron was postulated by Menzel[14] although this has not subsequently been established. An anhydrous perborate was claimed to have been made by evaporation under vacuum in the presence of excess hydrogen peroxide.[112]

Other compounds richer in oxygen include KBO_4,H_2O, first reported in 1912, of which a different form and a lower hydrate have recently been claimed[113], and an extensive series ranging from $KBO_4,0{\cdot}7H_2O$ to $KBO_{4{\cdot}9},0{\cdot}9H_2O$ made by Partington and Fathallah.[17–18] A compound with an active oxygen content corresponding to $KBO_{3{\cdot}7}$ was prepared by Tsal[114], who found that the crystal structure varied with the amount of active oxygen.

Similar highly oxygenated substances containing lower amounts of water, e.g., $KBO_4,0{\cdot}5H_2O$, $KBO_{3{\cdot}8}$, and $KBO_{4{\cdot}4},0{\cdot}1H_2O$ have been studied by Kazragis and Prokopcikas[62], who found them to have solubilities in water of under 1 g/litre at room temperatures and to possess thermal stabilities increasing as the ratio of active oxygen per boron rose to 2 and the hydration decreased.

Connor and Richards[23], from their NMR study of $KBO_{3{\cdot}7},0{\cdot}67H_2O$, concluded that this substance, like sodium perborate, was probably mainly a true hydrate.

Rubidium and Cæsium Perborates

Christiansen, in 1904, obtained $RbBO_3,H_2O$ and $CsBO_3,H_2O$, using alcohol to throw them out of aqueous reaction mixtures of the hydroxide, boric acid and hydrogen peroxide. Partington and Fathallah[17–18] similarly obtained a higher perborate with 2 to 2·4 atoms of active oxygen and 1·2 to $0{\cdot}5H_2O$ molecules per boron, i.e., approximating to $MBO_4,0{\cdot}5H_2O$.

Ammonium Perborates

$NH_4BO_3,0{\cdot}5H_2O$ can be prepared by methods similar to those used for the alkali compounds. In air it slowly breaks down to ammonia and oxygen; it explodes on heating in vacuo to 120°C.[12–13, 115]

Anhydrous NH_4BO_3 was prepared from the hydrate in 1900 by Constam and Bennett, by dehydration over phosphorus pentoxide, and by Kretzschmar[115] on vacuum drying. The latter author found that the anhydrous perborate had an *X*-ray pattern which could be distinguished from that of the hydrate, into which it could be reconverted without decomposition. (This difference in behaviour from sodium perborate is interesting.) Its solubility is 1·55% in water at room temperature.

Petrenko, in 1902, prepared the mono- and di-hydrates of NH_4BO_3,NH_4BO_4. More recently Tsal[114] made $NH_4BO_3,3NH_4BO_4$ and found that, as with the potassium perborates, the amount of active oxygen affected the structure. A patent[116] describes ammonium perborates containing two and three active oxygens per boron atom. Tanatar, in 1899, described a monohydrate, and Melikoff and Pissarjewsky, before 1900, prepared a hemihydrate with a molar ratio of ammonia to boron of two.[117]

Miscellaneous Perborates

Published work on perborates other than those of the alkali metals has for many years been sparse. Hence, there is little to add to Mellor, V, which mentioned the preparation of the perborates of copper, silver, the alkaline-earth metals, magnesium, zinc, monovalent thallium[118], nickel, cobalt and uranium, generally by double decomposition of an appropriate salt with sodium perborate. Ammonium perborate was used more recently by Tsal[114] for preparing the perborates of alkaline-earth metals, magnesium and beryllium. There have also been descriptions of preparations of calcium, magnesium[119] and barium[120] perborates in the patent literature.

A soluble material stated to contain active oxygen in approximately the same molar concentration as that found in perborates has been prepared from hydrogen peroxide and calcined alumina/boric oxide with the approximate composition $9Al_2O_3,2B_2O_3$. It is not clear whether a perborate was in fact formed.[121]

ANALYSIS OF PERBORATES

The principal interest in the analysis of perborates is the determination of the active oxygen content. Methods for this are generally based either on mutual reduction of peroxidic groups and potassium permanganate to give gaseous oxygen[76, 122–3], or on oxidation of iodide.

Trickett[124], in 1920, compared various methods and found that, using permanganate, direct titration gave low results, while both back titration of excess permanganate with oxalic acid and measurement of the evolved gaseous oxygen proved erratic. He found concordance between results obtained by methods based on oxidation of potassium iodide in hydrochloric acid solution, and the volume of oxygen evolved by reaction with calcium hypochlorite. Toul and Krasnec[125] found that a gasometric technique for evolved oxygen gave results lower than titration methods.

Subsequently, comparison of various well-known methods by Reichert, McNeight and Rudel[126] indicated that, in the absence of other oxidizing and reducing substances, titration with either permanganate, ceric sulphate or iodide were all dependable; these authors also found a potentiometric titration with sodium nitrite satisfactory for coloured solutions.

Errors due to permanganate oxidizing other components in detergent mixtures were stated by Milster and Meckel[127] to be minimized by addition of a mixture of phosphoric acid, sulphuric acid and manganese sulphate.

A recent British Standard[99] for the analysis of sodium perborate (and similar compounds) in detergents recommends two methods. One involves contacting the sample with manganous sulphate in dilute sulphuric acid prior to titration with potassium permanganate. In the other, the sample is acidified with warm, dilute sulphuric acid, ammonium molybdate and excess potassium iodide are added, and the liberated iodine is titrated against sodium thiosulphate, starch being used as indicator. The latter method is preferred when substances such as chelating agents are present, because these react with permanganate.

Ketova and Gusev[128] described a new procedure for various inorganic peroxidic compounds in which the perborate is reduced with ferrous ions in acid solution, the resulting Fe^{3+} is reduced by the leuco-base of methylene blue, and the methylene blue titrated with vanadium dichloride. Pilz and Johann[129] stated that the only method suitable in the presence of enzymes is reaction with titanium tetrachloride and colorimetric measurement of the peroxytitanate complex at 415 μ.

A colorimetric method involving reaction with dichromate and measurement of the absorption at 590 mμ is described by Garcia and Garrido.[130] Titration with hypovanadous salts is mentioned by Mittal, Tandon and Mehrotra.[131]

The borate content may be determined (after removing any organic matter, decomposing peroxy-compounds, and separating interfering ions such as phosphate and silicate) by titration of boric acid in the presence of glycerol or mannitol.[99]

Anomalous results are obtained for the water content of perborates when using Karl Fischer's method.[132]

USES OF SODIUM AND OTHER PERBORATES

Of the 300,000 to 400,000 tons of sodium perborate annually consumed in Europe, by far the greatest amount is accounted for by its use[133–8] as a bleach and stain remover, usually in detergent compositions for domestic laundering, which contain 10–30% of perborate. Considerable amounts are also used by the textile industry for similar purposes with a wide range of natural and synthetic fibres.[139–140]

Other substantial uses include: the oxidation and fixing of vat and sulphur dyes, where the borate also plays a part in securing bright colours[141]; denture cleansers, where the bubbles of oxygen evolved help to remove debris[142–3]; cosmetics preparations, which require mild bleaching or deodorizing action[144–5]; and cold permanent-waving preparations and other fibre setting materials, in which the perborate serves to oxidize ammonium thioglycollate.[146–8] In electroplating and metal finishing[149] sodium perborate is added to tin plating baths to oxidize sodium stannite, to nickel baths to prevent pitting[150], in zinc plating to improve the whiteness of the deposits[151], and in polishing baths.[152] In pharmacy, use has also been made of its mild disinfecting properties.[153–5] 'Effervescent perborates' are used for causing tablets to disintegrate on contact with water.

Uses in organic synthesis are apparently not widespread, but perborate may be used for making organic peracids; its use in improving the refining of maleic acid has been suggested.[156]

Sodium perborate has been described as a polymerization agent for monomers such as styrene, butadiene, methyl methacrylate, acrylonitrile and ethylene.[157–9] It also acts as a stabilizer for PVC.[160–4] Other suggested uses include: antichlor for removing hypochlorite[165] (with which it reacts quantitatively[97]), the preparation of chlorine dioxide[102, 166], the preparation of an iron catalyst for the hydrogenation of carbon monoxide[167], the regeneration of emulsions of oil and of paints[168–9], in the manufacture of paper[170–1], the improvement of lead–acid batteries by modifying the lattice of lead oxide[172], in sand moulds[173] and for the latensification of photographic emulsions.[174]

Calcium perborate, in particular, was found to have an unusually strong effect

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in driers for lithographic ink.[175] Lithium perborate was claimed to give, on firing, a ceramic bond which prevented water absorption by the coatings on welding electrodes.[176]

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SECTION A15

AMMONIUM BORATES

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GENERAL

Many ammonium borates quoted in Mellor, V, 80–1, have not been synthesized since and should be viewed with some suspicion. They include the following:

$(NH_4)_2O,2B_2O_3,2\frac{1}{2}H_2O$
$2(NH_4)_2O,B_2O_3,2H_2O$
$3(NH_4)_2O,4B_2O_3,3H_2O$
$3(NH_4)_2O,4B_2O_3,9H_2O$
$2(NH_4)_2O,5B_2O_3,5H_2O$
$(NH_4)_2O,3B_2O_3,7H_2O$
$(NH_4)_2O,6B_2O_3,9H_2O$

A material of composition $NH_4HB_4O_7,3H_2O$ has been distributed widely through laboratory supply houses and reference has been made to it in publications.[42, 64] No true compound of this ammonium hydrogen tetraborate composition exists, and the material is in reality a mixture of ammonium tetraborate and pentaborate.[46]

There remain three synthetic borates and two minerals which have been synthesized and which are well corroborated. These are listed below.

Minerals

$(NH_4)_2O,5B_2O_3,5\frac{1}{3}H_2O$ Ammonioborite

$$\left.\begin{array}{l}(NH_4)_2O,5B_2O_3,4H_2O\\(NH_4)_2O,4B_2O_3,4H_2O\end{array}\right\}\text{Larderellite}$$

Synthetic

$(NH_4)_2O,2B_2O_3,4H_2O$
$(NH_4)_2O,4B_2O_3,6H_2O$
$(NH_4)_2O,5B_2O_3,8H_2O$ (2 dimorphs)

Heller's paper[26] quotes the formation of three other ammonium borates including the only recorded anhydrous example, $[(NH_4)_2O,3B_2O_3]_n$. The hydrates are the 1:4:5 and 1:3:4 ammonium borates as well as the known 1:5:4 (larderellite). The synthesis of these borates was performed by the careful hydrolysis of borate esters with a little water in an organic solvent in the presence of ammonia. The type of product depended on the proportions of the reactants. The author also suggests structures for the various borates.[26]

The work on the system NH_3–B_2O_3–H_2O by Sborgi in the early 1920s, and before, remained unchallenged, except for some solubility data obtained by Menzel[1–2] until 1966, when Toledano et al. studied the system afresh. The 1924 edition of Mellor, V, 80 (1st line), contains a typographical error which can be confusing in relation to Sborgi's work. A formula of $(NH_4)_2O,B_2O_3,2\frac{1}{2}H_2O$ given as the solid phase of area bMc (Fig. 22) should read $(NH_4)_2O,2B_2O_3,2\frac{1}{2}H_2O$; no metaborate formation has yet been proved. It is also of interest in this context that no corrobora-

Refs. p. 691. Literature coverage is up to 1970

tion exists for the latter 'hemipentahydrate'. Its formulation by Sborgi has been explained by the analytical difficulty of differentiating between a compound of this formula and a compound in which the 1:2:4 ammonium borate hydrate has had part of its water of crystallization replaced by ammonia approximating to $(NH_4)_2O$,-$2B_2O_3$,$3H_2O$,NH_3. A compound of this latter composition was approached by treating the 1:2:4 borate, as a dry solid or aqueous slurry, with ammonia gas.[2] The products of these experiments were even treated with liquid ammonia, but *X*-ray analysis showed no change from the 1:2:4 pattern of the resultant products; there was only a slight increase in ammonia content, and certainly no metaborate formation. In conjunction with this work on attempted metaborate synthesis, a study of 1:1 NH_3/H_3BO_3 solutions up to 0·1 M showed that they behaved almost ideally, nearly complete hydrolysis taking place, but that at higher concentration boric acid started to form B_4O_7 ions, so that at no point could the solution be considered to contain ammonium 1:1 borate in the sense that it contained ammonium and monoborate ions in equivalent amounts.[3] Further work concerning the determination of cryoscopic and conductimetric data for solutions of 1:2 and 1:5 ammonium borates also showed extensive hydrolysis to NH_4OH and H_3BO_3.[4]

The recent studies of the NH_3–B_2O_3–H_2O system by Toledano[5] have shown a considerable enlargement of the area of stability at temperatures between 0° and 56° for the 1:4:6 ammonium borate hydrate compared with Sborgi's work. Reticular distances are tabled for the 1:4:6 and 1:2:4 borates.

Further work at 80° or 100° showed equilibrium between the 1:5:8 ammonium borate hydrate and its equilibrium solution to be metastable, the solid phase being 'ammonioborite' [$(NH_4)_2O$,$5B_2O_3$,$5\frac{1}{3}H_2O$] which precipitates after several hours' agitation at 100°.[6] Identification of the compound by *X*-ray diffraction patterns showed it to be identical with the mineral ammonioborite (*q.v.*). The ammonioborite curve was shown to be congruent to 10°C and to extend towards the ice curve. At 30°C or below the determination of equilibrium becomes difficult owing to the crystallization of a stable (at room temperature) dimorph of the 1:5:8 borate, the solubility branch of which lies between those of the metastable 1:5:8 borate and ammonioborite.[6]

Extensions of the system to include other salts have been studied. For instance, the solubility peak of the Na_2O–B_2O_3–H_2O system was widened by the addition of ammonia; the B_2O_3 solubility in the K_2O–B_2O_3–H_2O system increased but the alkali solubility decreased, and further solubility relationships in the system $(NH_4)_2O$–Na_2O–K_2O–B_2O_3–H_2O have been studied, especially in relation to pH.[7] Another relationship, when studying the effects of adding various H_3BO_3:KCl mixtures to ammonia solution, showed that ammonium borate somewhat contaminated with potassium chloride precipitated when the ratio was 2:1.[8] Because of complex borate formation, boric acid added to an ammonia solution retards the evaporation of ammonia; however, this is partially nullified by the addition of polyhydroxy-compounds such as sucrose, mannitol, etc.[9]

The syntheses of B–N compounds in general from boric acid have been discussed[10] and a recent survey of the synthetic procedures for B–N compound formation with a comprehensive listing of compounds and physical properties is useful.[11] As well as the latter references on synthesis, further work on the behaviour of ammonia and volatile amines on boric acid may be referred to.[12] Ammonium borates in general react in excellent yield with C_2–C_6 alcohols to give $B(OR)_3$ esters, ammonia and water, which is azeotroped with alcohols or other entrainers.[13] The polarizability and bond energy of B–N compounds have been determined.[14] The Raman spectra of ammonium borates, compared with alkyl borates, show a characteristic frequency in both, probably explained by the similarity of the BO_3^{3-} ion group and $B(OR)_3$.[15]

Calcium borate ores react with carbo-ammoniacal liquors to give ammonium borate solutions, which in turn may be treated with greater than 50% of the stoichiometric quantity of soda under distillation conditions, when virtually all the ammonia is lost, giving a starting solution for sodium borate production.[84]

$(NH_4)_2O,2B_2O_3,4H_2O$

The 1:2:4 borate exists congruently with its own solution in the $(NH_4)_2O$–B_2O_3–H_2O system, a fact confirmed but modified by recent studies.[5–6] Reticular distances for this compound as well as the 1:4:6 borate for the 0°, 10°, 20°, 30° and 56°C isotherms have been tabulated.[5] The formation of this compound from boric acid and ammonia in aqueous solution is described[2] and a noticeable ammonia tension observed. Synthesis of this borate out of contact with water has also been shown possible, powdered boric acid being reacted with ammonia in the dry state, with a B/NH_3 ratio of 4·5. However, if this ratio is increased to $\geqq 5{\cdot}0$, the pentaborate $(NH_4)_2O,5B_2O_3,8H_2O$ forms.[28] The same reactions take place in methyl cyanide at room temperature, the tetraborate being formed if the solution is saturated with ammonia.[29]

A ternary system $(NH_4)O,2B_2O_3$–$Na_2O,2B_2O_3$–H_2O was studied from the cryohydric point to 65°C, but at temperatures above 40°C the study was difficult owing to loss of ammonia.[30] The 1:2 borate is of theoretical interest when it reacts with sodium sulphate:

$$(NH_4)_2O,2B_2O_3 + Na_2SO_4 = Na_2O,2B_2O_3 + (NH_4)_2SO_4$$

This is the only known case where the theory of reciprocal pairs may be applied completely to a double decomposition. During this study, polythermic diagrams were composed, invariants of the system fixed thermometrically, and zones in which there are stable two-salt pairs defined.[31]

As already mentioned, treatment of the 1:2:4 borate with liquid ammonia or ammonia under pressure gives a product which approaches $(NH_4)_2O,2B_2O_3,3H_2O,NH_3$[2–3]; this probably accounts for some peculiar ammonium borate formulations. The 1:2:4 borate also reacts with various metallic salts to give double salts which are referred to in detail under the sections relating to the parent metal borate. As an example, it reacts with boric acid and zinc sulphate in aqueous solution, crystallizing over a period of 1–4 days at 40°C to give a product of the formula $(NH_4)_2O,ZnO,6B_2O_3,10H_2O$ having a density of 1·9 g cm^{-3}.[32] Unpublished work has shown that the 1:5:8 and 1:2:4 borates when mixed dry result in formation of a cake of the 1:4:6 borate with the release of two molecules of water of crystallization.

$$\begin{aligned}&(NH_4)_2O,2B_2O_3,4H_2O + 2[(NH_4)_2O,5B_2O_3,8H_2O]\\&\qquad = 3[(NH_4)_2O,4B_2O_3,6H_2O] + 2H_2O \qquad \text{(Ref. 33)}\end{aligned}$$

The borate has a density of 1·58 g cm^{-3}. It is not completely stable at atmospheric pressures and normal temperatures, smelling somewhat of ammonia. 0·1–10% solutions show little variation of pH, which remains at about 8·8. The ^{11}B NMR chemical shift value for $(NH_4)_2O,2B_2O_3,4H_2O$ has been determined and found to be $-10{\cdot}3$, cf. borax, $-8{\cdot}9$.[35] It is suggested that the structure of the compound belongs to the class of insular borates containing independent double-ring polyions and empirically described as $(NH_4)_2B_4O_5(OH)_4,2H_2O$, (*v.* borax).[36]

$(NH_4)_2O,4B_2O_3,6H_2O$

Little is known of this compound, although it is a solid phase of the $(NH_4)_2O$–B_2O_3–H_2O system. Recent workers[5] have shown its area of existence to be larger than Sborgi's original work (Mellor, V) indicated. It crystallizes from a solution of ammonia and boric acid with a N/B ratio somewhat greater than 4.[43] The structural formula of the 1:4:6 borate has been studied[44] and can be represented as $(NH_4)_2B_8O_{10}(OH)_6,3H_2O$, belonging to the class of insular borates containing mixed polyions.[36]

$(NH_4)_2O,5B_2O_3,4H_2O$ $[(NH_4)_2O,4B_2O_3,4H_2O]$ (Larderellite)

The formula in brackets above is the formula given to larderellite by its discoverers, Bechi and Rose (Mellor, V). This has now been shown to be incorrect, and $(NH_4)_2O$,-

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$5B_2O_3,4H_2O$ proved correct. The matter is further confused in that it was once reported to be a dimorph (together with ammonioborite) of the 1:5:8 borate.[45] Synthesis of this mineral had not been performed until the 1960s and then only via an organic solvent phase. Careful hydrolysis of borate esters dissolved in an organic solvent in the presence of a little water and ammonia gave a number of ammonium borates (*q.v.*) depending on the proportions of the reactants, one of which was synthetic larderellite.[26] In the same year other workers produced the same compound by passing 1 mol of ammonia gas into a saturated boiling solution containing 5 mol of boric acid in acetonitrile or dioxane and then diluting with ether.[29] If no dilution occurred the 1:5:8 borate was formed.

Several *X*-ray crystallographic studies have been made of larderellite. Marinelli[51] found it to be monoclinic, with space-group $P2_1/c_1$, $a=9{\cdot}47$, $b=7{\cdot}63$, $c=11{\cdot}65$ Å (all $\pm 0{\cdot}01$ Å), d (calc.) 1·95 and $Z=2[(NH_4)_2B_{10}O_{16},5H_2O]$. Clark[48] confirmed the cell and space-group but changed the orientation: $a=11{\cdot}63$, $b=7{\cdot}61$ and $c=9{\cdot}44$ Å ($\pm 0{\cdot}03$ Å), with determined density of 1·905. Later work[47] exactly confirmed Marinelli's lattice parameters and suggested that the unit cell contained four stoichiometric units, $NH_4B_5O_8,2H_2O$.

Previous examination suggested a double-ring chain borate of basic structure $NH_4^+[B_5O_6(OH)_4]^-$.[43] Later work on the β-phase crystal confirms this double-ring polyion, assigning it as monoclinic, space-group $C2/c$, with lattice constants $a=11{\cdot}65$, $b=8{\cdot}66$ and $c=11{\cdot}40$ Å, with d (expt.) $=1{\cdot}59$.[49] (See also [60].)

$(NH_4)_2O,5B_2O_3,5\frac{1}{3}H_2O$ (Ammonioborite)

This mineral is distinct from larderellite but has in the past been claimed to be a dimorph of it[50] and also of the synthetic 1:5:8 borate.[45] Somewhat surprisingly it has recently been produced synthetically, having been found as stable phase in the $(NH_4)_2O$–B_2O_3–H_2O system, congruous with its solution from 100° to 10°C. For instance, ammonioborite is precipitated after stirring a saturated solution of the 1:5:8 borate at 100°C for several hours.[6] There is a little confusion concerning the structure. It is postulated that the compound has the pentaborate ion structure also found in ammonium and potassium 1:5:8 borates, i.e. $[B_5O_6(OH)_4]$.[43] Alternatively, as with larderellite, a chain structure containing double rings giving the ion $[B_5O_7(OH)_2]$ has been suggested.[36] From *X*-ray single-crystal analysis the most probable space-group is $C2/c$, with $a=25{\cdot}27\pm 0{\cdot}5$, $b=9{\cdot}651\pm 0{\cdot}3$, $c=11{\cdot}56\pm 0{\cdot}03$ Å, d (calc.) 1·758, d (observed) $1{\cdot}765\pm 0{\cdot}004$.[60]

$(NH_4)_2O,5B_2O_3,8H_2O$ (Ammonium Pentaborate)

More work has been done on this compound than on any of the other ammonium borates, probably because it is easily prepared and stable. For some time the evidence pointed towards a stable equilibrium between the octahydrate and its solution. However, a series of solubility studies on the $(NH_4)_2O$–B_2O_3–H_2O system, allowing long periods of time for equilibrium to be established, showed it to be metastable[6] (see ammonioborite). In addition, the same workers showed that at 30°C and below, the ammonioborite and the metastable 1:5:8 borate curves were bisected by a curve representing a dimorph of the 1:5:8 borate, making the determination of equilibrium difficult. This new dimorph, or β-form, has more recently been formed by stirring a saturated solution of the metastable 1:5:8 borate (α-form) for 10 days at room temperature.[52] The long periods that are needed in this system for reaching equilibrium are characteristic of many borate systems, accounting for some confusion in solid phase definition in the past and for statements such as: 'Solubility studies had been carried out on the above system $(NH_4)_2O$–B_2O_3–H_2O showing no breaks in the curve, indicating no further hydrate formation between 0° and 40°.'[53]

Powdered boric acid reacts with ammonia at room temperature, if the $B:NH_3$ ratio is greater than 5:1, to give the pentaborate.[28] It also reacts in this way if it is suspended in methyl cyanide and treated (but not saturated) with ammonia gas.

Boric acid in a powdered form reacts with formamide, without free ammonia, to give the pentaborate and formic acid.[55] It may also be prepared by reacting borax with ammonium chloride.[56] The two compounds are heated together in aqueous solution until the liberated ammonia is removed. Crystals of ammonium pentaborate octahydrate are then obtained after concentrating the residual solution. Other methods of pentaborate formation are known; for instance, calcined calcium borate ores such as colemanite react with ammonium sulphate at 95°–105°C, producing calcium sulphate and ammonia as by-products. The calcium sulphate and gangue are removed by filtration, leaving a solution of ammonium pentaborate which may be either crystallized or reacted with ammonium bisulphate to give boric acid and ammonium sulphate, which may be re-cycled.[54]

$(NH_4)_2O,5B_2O_3,8H_2O$ dehydrates at 150°C, losing all but 2 mol of water and less than 1% of ammonia. At 200°C and 1 mm pressure a further 0·85 mol of water is lost and about 2% of the ammonium radical.[33] If heated at a sufficiently high temperature all the ammonia and water are expelled to give boric oxide.[56]

The pentaborate produces esters $B(OR)_3$ ($R = Et$, Pr, *i*-Pr, Bu, Am) in good yield by reaction with the appropriate alcohol, the water being azeotroped with excess alcohol or an entrainer.[13] It also reacts with various salts to produce less soluble borates, e.g. with strontium nitrate or iodate, forming the strontium isomorph of colemanite, $2SrO,3B_2O_3,5H_2O$, as well as the 1:1:4 and 1:3:5 strontium borates.[57]

It has been confirmed that ammonium pentaborate octahydrate forms orthorhombohedric crystals, according to goniometric and optical observations.[58] It has a density of 1·567 g cm^{-3}.[43] The elementary cell consists of four molecules, and the crystal parameters are given as $a = 11{\cdot}09$, $b = 11{\cdot}28$, $c = 9{\cdot}27$ Å[59], which are only in slight variance with the original work by Rammelsberg (ref. Mellor, V). The ammonium salt, as with its isomorphous potassium analogue, contains the pentaborate ion $[B_5O_6(OH)_4]^-$ according to *X*-ray data.[60] More recently an N.M.R. single-crystal study has been carried out, assigning the formula $NH_4(B_5O_{10}H_4),2H_2O$.[61] A study of the crystal structure of the *β*-phase of the pentaborate has been made.[49] A review of work up to 1957 of the crystallographic, elastic and piezoelectric properties of the pentaborate discusses the various conflicting data.[62] Some five years later the compound was restudied, and the dielectric constant was shown to be temperature-dependent. It was determined in three planes perpendicular to the crystal axes between −200° and 150°C. The same workers also investigated anew the modulus of elasticity and the electromechanical coupling coefficient, and derived the piezoelectric modulus. They found that the piezoelectric property was lost irreversibly by partial dehydration, i.e. the loss of two of the molecules of water of crystallization.[58] Other physical properties studied were the compression characteristics up to 40,000 kg cm^{-2} [63] and the heat capacity at 15°–370° K. However, the results at the higher temperatures were thought to be affected by dehydration. Various solution properties of the 1:5:8 ammonium borate have been studied. Supersaturated solutions are easily formed, and as a corollary the rate of crystallization is proportional to the extent of supersaturation.[53] The solubility is 70·3 g of anhydrous pentaborate per 1000 g of water at 18°C, and 87·2 g/1000 g at 20°C.[2] With the recent studies of the NH_3–B_2O_3–H_2O system showing that it is not as Sborgi originally believed, the solubility data published prior to 1966 must be considered as having been obtained under conditions of metastable equilibrium.[5] The pH of pentaborate solutions decreases slightly with increasing concentration, e.g. 0·1%, pH 8·48; 10·0%, pH 7·32. The electrical conductivity and pH have been studied at 20°–40°C.[53] Ammonium pentaborate with dimethyl formamide (DMF) replacing some of the water of crystallization, $(NH_4)_2O,5B_2O_3,4H_2O,2DMF$, is formed by introducing ammonia gas into a boiling solution of metaboric acid in dimethylformamide.[29]

Mixed Borates containing the Ammonium Radical

Ammonium metal borates of a number of elements have been produced in an analogous fashion to the corresponding potassium salts, simply by crystallizing the amorphous precipitate formed by reacting in solution a metal salt, ammonia and boric acid.[69] Further details of each salt so formed are found under the section dealing with the metal borate involved. However, a short list of the well-substantiated compounds may be of value here.

Magnesium	$(NH_4)_2O,MgO,3B_2O_3,15H_2O$ $(NH_4)_2O,MgO,3B_2O_3,7H_2O$	(Ref. 70)
Calcium	$(NH_4)_2O,CaO,4B_2O_3,12H_2O$	(Ref. 69)
Zinc	$(NH_4)_2O,ZnO,6B_2O_3,10H_2O$	(Ref. 71)
Manganese	$(NH_4)_2O,MnO,6B_2O_3,11H_2O$	(Ref. 69)
	$3(NH_4)_2O,2MnO,B_2O_3,4C_4H_4O_5$ (Tartrate)	(Ref. 72)
Cobalt	$(NH_4)_2O,CoO,6B_2O_3,11H_2O$	(Ref. 73)
Nickel	$[Ni(NH_3)_6]B_6O_{10},2(NH_4)_2B_4O_7,12H_2O$	(Ref. 74)
	$[Ni(NH_3)_4]B_4O_7,(NH_4)_2B_4O_7,12H_2O$	(Ref. 75)

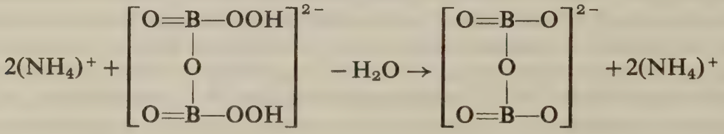
In addition to these compounds the system boric acid–ammonium metavanadate–water has been studied recently at various temperatures.[76] An ammonium borate containing a mucate anion has also been formed by mixing solutions of boric and mucic acids and treating the product with ammonia. The addition of alcohol causes the precipitation of $3(NH_4)_2O,B_2O_3,2C_6H_8O_7,3H_2O$ which has a solubility of $49{\cdot}4$ g l^{-1}.[77] Analogous ammonium *bis*(ascorbato) borates $3(NH_4)_2O,B_2O_3,4C_4H_8O_6,6H_2O$ have been produced from alcoholic solutions of boric acid and L-ascorbic acid in molar ratio 1:2 by precipitation with ammonium hydroxide.[83]

Ammonium Perborates and other Peroxy-Salts

Ammonia apparently forms a true perborate analogous to potassium perborate.[27] It liberates iodine alone from a potassium iodide solution (Reissenfeld test) and may be represented as $NH_4BO_3,\frac{1}{2}H_2O$.

The structure of perborates appears to be open to much conjecture; further discussion of the designation of perborates and peroxidated borates will be found in the section on perborates (*q.v.*). The formation of the above-mentioned perborate has been carried out by the reaction of 25 g of 15% ammonia solution on 250 cm³ of 3% hydrogen peroxide containing $12{\cdot}4$ g of boric acid, and precipitating the product with 500 cm³ of alcohol.[27] In the presence of non-acid desiccants the compound is stable; however, on drying at 50°–55°C ammonia and half of the water are lost. Further heating in vacuum above 115°C causes explosive decomposition.[27]

The peroxy anhydride can be formed by controlled dehydration and is formulated as $(NH_4)_2O,B_2O_3,O_2$[78] having a distinct Debye-Scherrer pattern similar to that of the original hemi-hydrate. The following structural explanation of the dehydration was postulated[79], although current views do not support it (see Perborates).



$$2(NH_4)^+ + \left[\begin{array}{c} O{=}B{-}OOH \\ | \\ O \\ | \\ O{=}B{-}OOH \end{array}\right]^{2-} - H_2O \rightarrow \left[\begin{array}{c} O{=}B{-}O \\ | \\ O \\ | \\ O{=}B{-}O \end{array}\right]^{2-} + 2(NH_4)^+$$

The production of an anhydrous perborate, $(NH_4)_3BO_3$, by the treatment of equimolar quantities of hydrogen peroxide and boric acid with excess of ammonia is described in a patent.[80] A much higher proportion of peroxide can be used, and the solution crystallized at 5°–10°C to obtain the diperoxyhydrate $NH_4BO_2,2H_2O_2$.[81–2]

Uses of Ammonium Borates

Ammonium borates have found application in a variety of fields. A major and well-established use is as an electrolyte constituent for electrolytic condensers.[65] The anodizing of aluminium, tantalum, titanium and zirconium foil in an ammonium 1:2 borate solution with the formation of an oxide film is a technique which has been patented for the reduction of leak characteristics of capacitors.[37] Another patent claims unproved low-temperature characteristics for capacitors by curing the foils in boric acid/ammonium 1:2 borate solutions at 520 V.[38]

An anodic double-layer oxide film may be formed on metallic titanium from non-aqueous solutions of ammonium borate in mono- or polyhydric alcohols or polyhydric ethers.[17] A recent patent suggests mixed solutions containing ammonium borates, acetates, citrates or tartrates of maximum electrical conductivity rather than the simple salt.[16] A suitable layer on titanium is not obtained if the electrolytic solution has an aqueous base.[18] Zirconium may also be anodized in the presence of ammonium borate, but the use of boric acid as an electrolyte is preferable as it imparts the property of halting oxidation by high-pressure steam.[19]

The buffering nature of ammonium borate solution is probably its function in the addition to alkylarenesulphonates to stabilize their colour.[20] Its use in 0·01 N solution at pH 9·0 was found to be the best eluent for the removal of tetracycline and oxytetracycline antibiotics from cation-exchange resins.[21]

Borates are used as preservatives and fungicides which accounts for the screening of ammonium borates in the control of cork spot in d'Anyon pears, a trial that was unsuccessful.[22] It is also used as a rubber latex preservative.[23] Two further uses of ammonium borates are based on the fact that heat decomposes them to boric oxide with the evolution of ammonia and that, in addition, they tend to absorb carbon dioxide at high temperatures. In the first case a spray of ammonium borate on to glass with subsequent heat treatment provides a source of boric oxide which makes the glass resistant to alkali-metal vapour.[24] Secondly, hard pellets of fine moist iron suitable for use in blast furnaces may be made by mixing with small percentages of calcium or magnesium oxides or hydroxides together with ammonium borate or borax, added to solubilize carbon dioxide which has the property of hardening the pellets.[25] Another suggested metallurgical use is in the control of 'hot ground' in copper-ore deposits.[64] Ammonium borates were found to be the best inhibitors for spontaneous combustion of sulphide-rich ores.[64]

A water-soluble dry casein mixture suitable for texture paints and cements is prepared by dry blending casein with an ammonium salt, the ammonium 1:2 borate being preferred.[39] Both the 1:2 and 1:5 ammonium borates give stability to liquid laundry starch.[40] The 1:2:4 ammonium borate hydrate has been used in admixture with magnesium carbonate, magnesium fluoride and titanium oxide after heating at 450°C to produce a material with blue-white fluorescence.[41] It has also been tried as a corrosion inhibitor for ammonium nitrate solutions, but is less successful than alkali-metal borates[42]; '$NH_4HB_4O_7,3H_2O$', mentioned in this patent is in reality a mixture of the tetra- and penta-borates. It also has fire-proofing properties[54] and is used in paper-coating compositions.[34] It has been patented as a constituent of a soldering flux[66] and acts with citric acid as a binder in magnesia refractory hearths.[67] The pentaborate is also a convenient co-constituent of a glass composition which has an ultra-violet transmittance of 89·3% that of fused silica, but a fusion temperature of only 1250°C.[68] 'Ammonium perborate'—(NH_4BO_2,-$2H_2O_2$) is described as a bleach for laundering.[81–2]

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SECTION A16

SUBSTITUTED AMMONIUM BORATES AND RELATED COMPOUNDS

BY G. H. BOWDEN

The class of compounds listed under this heading is essentially that described by the general ammonium borate formula:

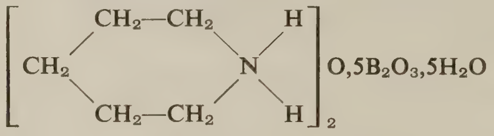
$$[NH_4]_2O,xB_2O_3,yH_2O,$$

but with the hydrogen atoms of the ammonium radical replaced partially or completely by like or differing organic or —NH_2 groups:

e.g.

$$[(CH_3)_{4-n}NH_n]_2O,5B_2O_3,xH_2O \qquad (n = 0,1,2,3)$$

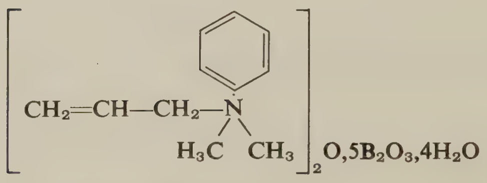
$$[(CH_3)_{4-n}(C_2H_5)_nN]_2O,5B_2O_3,xH_2O \qquad (n = 0,1,2,3,4)$$



(piperidinium pentaborate)

$$[(NH_2)_2{=}C{=}NH_2]_2O,2B_2O_3,4H_2O$$

(guanidinium diborate)



(allyldimethylanilinium pentaborate)

Alkanolamine borates (which are in fact esters of boric acid), hydrazine borate and boranilide are also included in this review.

1. Amine Borates

Most of the work on amine borates has been carried out since about 1940, the first serious study having been made by Ferrari et al.[1] on the preparation of the series $[(CH_3)_{4-n}(C_2H_5)_nN]_2O,5B_2O_3,xH_2O$, where $n=0$, 1, 2, 3 or 4 and $x=4$ or 5, by the addition of aqueous solutions of boric acid to the appropriate bases. These authors were unable to prepare tetra-alkyl ammonium diborates, such as those described by Milbauer[2] in 1913, inferring that they were probably too soluble to be isolated. By far the largest number of amine borates are of the 1:5 type, though borates of the 1:1, 1:2, 1:3, 1:4 and 1:6 types have been reported.

1:1 Borates

Choline or trimethylamine glycol reacts with 1–3 moles of boric acid and after concentrating the mixture under reduced pressure, choline borate

$$[(CH_2OH.CH_2)N(CH_3)_3]_2O,B_2O_3,2H_2O$$

is formed; after dissolution of the reaction mixture in alcohol the salt is precipitated with acetone or other organic solvent in which it is insoluble.[3] Alternatively, the original reaction may be performed in alcoholic solution and the product precipitated with acetone, etc. It is a white, microcrystalline material which melts above 300°C, and is alkaline in solution.[3] This compound appears to be the only well substantiated metaborate, although reactions between boric acid and pyridine; 2-picoline, 3-picoline, 4-picoline, 2,3-lutidine, 2,4-lutidine, 2,6-lutidine, 2,4,6-collidene, quinoline, *iso*quinoline, piperidine and pyridine-cyanuric acid, respectively, produce compounds approximating to derivatives of metaboric acid. *X*-Ray analyses of these compounds gave data which suggested a layered structure of alternate sheets of HBO_2 (metaboric acid) and the base; the densities and lattice constants were determined for these compounds.[4] Other compounds which have the structure $[B(OR)_2]_2$,en, where en = ethylene diamine, can be considered here, as the B:N ratio is 1:1. Three of these complexes,

$[B(OMe)_3]_2$,en m.p. 80°C
$[(OEt)(OMe)_2B]_2$,en
$[(OPr^i)(OMe)_2B]_2$,en,

have been produced by reaction of trimethyl borate, triethyl borate or tri-*iso*propyl borate with ethylene diamine in methyl alcohol. It is interesting to note that the investigators were unsuccessful in producing the simple complexes of ethylene diamine with triethyl borate or tri-*iso*propyl borate, a fact ascribed by them to the electron-repelling effect of the alkyl groups.[5] These reactions are exothermic.

1:2-Borates

Guanidine derivatives of boric acid fall into the amine borate classification, 1:2- and 1:5-borates having been synthesized. The 1:2-borate is formed from guanidinium carbonate and boric acid (theoretical quantities) in a minimum of water at 90°C; after evolution of carbon dioxide and further dilution, white crystals of $[(NH_2)_2{=}C{=}NH_2]_2O,2B_2O_3,4H_2O$ crystallize.[6] It is also suggested that this compound may be produced from guanidine chloride and borax.[7]

Apart from Milbauer's unconfirmed early work resulting in the production of a tetra-alkylamine ammonium biborate[2], the only other 1:2-amine borate prepared and described as such is cyclohexylamine biborate, $[C_6H_{11}NH_3]_2O,2B_2O_3,H_2O$. This may be made in the usual manner by reacting boric acid with an excess of cyclohexylamine in an organic diluent at 60°C according to the following equation[8]:

$$2C_6H_{11}NH_2 + 4H_3BO_3 \longrightarrow (C_6H_{11}NH_3)_2O,2B_2O_3,H_2O + 4H_2O.$$

Water produced in the reaction is a disadvantage in industrial production, as it increases in amount during re-cycling of liquors and causes hydrolysis. This build-up may be avoided by the use of metaboric acid or, more economically, equimolar amounts of boric acid and boric oxide.[9] Three moles of cyclohexylamine are gently refluxed for 2 hr with one mole each of boric acid and boric oxide; the liquid is cooled and then heated to 70°C *in vacuo* to give the desired product in almost quantitative yield.

Cyclohexylamine biborate is a white crystalline material about 29% soluble in water at 30°C, with hydrolysis, and 5% soluble in ethanol. It starts to decompose when heated above 120°C, losing both amine and water and leaving a residue of boric oxide. It also decomposes extremely slowly at 80°C, and even at room temperatures it loses some amine. Reaction of the amine with carbon dioxide from the air is a driving force and advantage may be taken of this phenomenon, cyclohexylamine biborate being used as an alternative to the carbonate as a vapour phase corrosion inhibitor. A 10% 'solution' in water has a pH of 9·6 at 25°C.[15]

1:3-Borates

The only reference to N-substituted ammonium triborates suggested that the major factors governing the formation of a triborate or pentaborate are the steric requirements of the amine and the molar ratio of the reactants. The structure of these compounds has been discussed.[10]

1:4-Borates

Dodecylamine and octadecylene-amine are reported to form 1:4-borates when treated at 90–100°C with boric acid in aqueous solution, with vigorous agitation.[6] Their respective formulae have been given as:

$$[C_{12}H_{25}NH_3]_2O,4B_2O_3,9H_2O$$
$$[C_{18}H_{35}NH_3]_2O,4B_2O_3,6H_2O$$

They were evaluated as preservatives in the citrus industry.[6] By standard methods of preparation, as described for cyclohexylamine-1:2-borates, but altering the proportions of the reactants, the cyclohexylamine-1:4-borate is formed,

$$(C_6H_{11}NH_3)_2O,4B_2O_3,7H_2O.$$

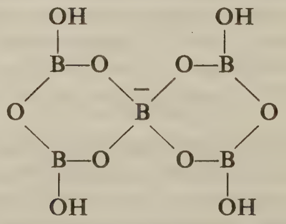
It has similar properties to the 1:2-borate but is more stable and can be recrystallized from water. A 10% solution has a pH of 8·1.[16]

1:5-Borates

Amine pentaborates are the most stable and well investigated of this group of compounds. The following compounds were produced[1] by precipitation from a boiling aqueous mixture of boric acid and the appropriate alkylammonium base:

$$\left.\begin{array}{l}[(CH_3)_4N]_2O,5B_2O_3,nH_2O\\ [(CH_3)_3(C_2H_5)N]_2O,5B_2O_3,nH_2O\\ [(CH_3)_2(C_2H_5)_2N]_2O,5B_2O_3,nH_2O\\ [(CH_3)(C_2H_5)_3N]_2O,5B_2O_3,nH_2O\\ [(C_2H_5)_4N]_2O,5B_2O_3,nH_2O\end{array}\right\rangle n = 4 \text{ or } 5$$

The authors[1] state that they were unable to decide whether n was 4 or 5; in later work[6] it was found on analysis that the hydration of the first and last of the above compounds was closer to $n=5$. On the basis of elemental analysis of the tetra-methyl and -ethyl amine borates, formed by mildly heating the tetra-methyl or -ethyl ammonium hydroxide with ammonium pentaborate in aqueous solution, *in vacuo*, n was indicated to be much nearer to four.[25] These borates displayed unique properties when used as constituents in the electrolyte system of electrolytic capacitors.[12] They are usable in a variety of organic solvents, which is an advantage over the unsubstituted ammonium borates. In addition to the tetra-methyl and -ethyl compounds the patent[12] describes quaternary ammonium pentaborates of the general formula $R_1R_2R_3R_4N,H_4B_5O_{10}$, where R_1, R_2, R_3, R_4 are organic radicals and $H_4B_5O_{10}$ is a pentaborate ion with suggested structure



In particular the tetra-allyl, allyldimethylanilinium and fluorenyltrimethyl ammonium pentaborates were described. These were formed from the respective amine halide by treatment with silver oxide and the subsequent reaction of the base with boric acid in a 1:5 molar ratio.[12] Other amine pentaborates have been produced and given the general formula $Q,H_4B_5O_{10},nH_2O$ or $Q_2O,5B_2O_3,4H_2O$. It is suggested that the size and symmetry of the quaternary ammonium ion dictates the nature of the spaces in the crystal lattice and that the nature of spacing determines how many, if any, molecules of water will crystallize with the salt, or whether boric acid molecules will be occluded[25] (see below under Hexaborates).

Reference was made above to the possible use of amine borates in citrus fruit preservation.[6] Other borates investigated for this purpose were:

Piperidine pentaborate pentahydrate, $(C_5H_{10}NH_2)_2O,5B_2O_3,5H_2O$;
Hexadecylamine pentaborate pentahydrate, $(C_{16}H_{33}NH_3)_2O,5B_2O_3,6H_2O$;
Octadecylamine pentaborate hydrate (hydration not determined),
$(C_{18}H_{37}NH_3)_2O,5B_2O_3,xH_2O$;
Guanidinium pentaborate hexahydrate, $[(NH_2)_2C=NH_2]_2O,5B_2O_3,6H_2O$;
Cetyltrimethylammonium pentaborate pentahydrate,
$[C_{16}H_{33}N(CH_3)_3]_2O,5B_2O_3,5H_2O$.

Guanidinium pentaborate was formed from the carbonate and the theoretical quantity of boric acid, in the same way as the diborate. Cetyltrimethylammonium pentaborate was prepared from the bromide via the base by treatment with alcoholic potash and then reaction with boric acid. The guanidinium borate can also be prepared from a mixture of borax and boric acid by treatment with guanidinium chloride.[6]

Methyl- and ethyl-substituted ammonium borates prepared from boric acid and a 10–15% excess of amine were shown to be difficult to recrystallize from water even at 50–60°C, owing to appreciable loss of the bases by volatilization.[13] The authors postulate reasons for the fact that ammonium borate and the methylammonium pentaborates are octahydrated, whereas the higher-substituted ammonium pentaborates are normally tetrahydrated, e.g.:

$(NH_4)_2O,5B_2O_3,8H_2O$
$(MeNH_3)_2O,5B_2O_3,8H_2O$
$(Me_2NH_2)_2O,5B_2O_3,4H_2O$
$(Me_3NH)_2O,5B_2O_3,4H_2O$
$(EtNH_3)_2O,5B_2O_3,4H_2O$
$(Et_2NH_2)_2O,5B_2O_3,4H_2O$
$(Et_3NH)_2O,5B_2O_3,4H_2O$

The decrease in hydration was explained by changes in the capacity of the cation to become hydrated; these changes were attributed to decrease in electrostatic character related to the increase in ionic diameter caused by introducing alkyl radicals.[13] Dimethylammonium pentaborate is able to complex two molecules of dimethyl formamide (DMF), giving colourless crystals which have the constitution $(Me_2NH_2)_2O,5B_2O_3,4H_2O,2DMF$.[14] It is produced by reacting metaboric acid or boric acid with dimethyl formamide at temperatures up to the boiling point of the latter.

1:6-Borates

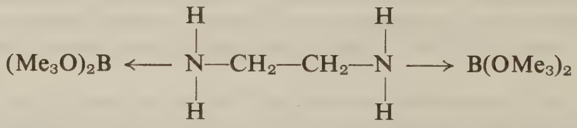
Certain amines (viz. cinnamyltriethylamine, benzyldimethylallylamine and benzyldimethyl-*n*-propylamine) form hexaborates which have been given the general formula $Q,H_4B_5O_{10},H_3BO_3$ (Q = cinnamyltriethylammonium, benzyldimethylallylammonium or benzyldimethyl-*n*-propylammonium radicals), implying a pentaborate ion with a more or less loosely bound boric acid molecule.[15] This may be arguable, but can be represented using the oxide formulation as $Q_2O,6B_2O_3,7H_2O$. The patent claims that the resulting hexaborates can be used for the same purposes as certain complex amine pentaborates (*q.v.*[12]). Apart from a hydrazine hexaborate (see below) the only other recorded amine hexaborate is triethylammonium hexaborate, $(Et_3NH)_2O,6B_2O_3,6H_2O$, prepared as a potential citrus fruit preservative, as were some of the previous borates mentioned.[6]

Less Well-defined Amine Borates

By the strict definition of an amine borate used here, none of the following compounds should qualify. However, it is appropriate to deal with the following categories of associated compounds:

Amine–borate ester addition compounds;
Compounds containing both —OH and —NH_2 or substituted ammonium groups;
Boranilides;
Borate-specific ion-exchange resins and other polymers;
Alkanolamine borates;
Hydrazine borates.

Borate esters form well-defined addition compounds with certain amines. Ethylenediamine reacts vigorously with a boron methoxide–methanol azeotrope to form a crystalline compound melting at 80°C having the formula $B[O(CH_3)_3]_2$,en.[5,18] Efforts to prepare the corresponding ethyl and *iso*propyl analogues were unsuccessful. However, the methyl/ethyl and methyl/*iso*propyl addition compounds were formed from the ethyl or *iso*propyl borate in methanol and ethylene diamine The standard formulae correspond to:



$$(Me_3O)_2B \longleftarrow \overset{H}{\underset{H}{N}}—CH_2—CH_2—\overset{H}{\underset{H}{N}} \longrightarrow B(OMe_3)_2$$

As well as diamines, addition compounds are formed between single-nitrogen compounds, e.g. ethylamine, pyrrolidine and piperidine, and triethyl or tri-allyl borates. The ^{11}B N.M.R. chemical shifts of these compounds are dependent on reactant concentrations, which indicates that exchange occurs.[18]

Boric acid reacts with polyols, such as ethylene glycol, mannitol, etc., to give a compound with stronger acidic properties than has boric acid itself. It is therefore not surprising that these compounds react easily with amines. Such a compound, in this case an amine/ethylene glycol/boric acid complex, has been used to catalyze the reaction between fatty oils and sulphur. The reaction takes place at 150°C over a period of 1–3 hr.[19] It has also been shown that compounds highly soluble in aqueous and organic solvents are produced from carbohydrates such as mannitol, sorbitol, raffinose, rhamnose, sorbitan, dextrose or hydroxyethyl cellulose after reaction with boric acid and, subsequently, certain amines. The amines referred to in this work[20] were procaine, benzocaine, sulphanilamide, metol sulphate, caffeine, nupercaine, pontocaine, butyn, eucupine and epinephrine. It is claimed that boric acid reacts with aromatic or aliphatic compounds containing —OH and —CO_2H groups separated by no more than two carbon atoms, and that the product combines with amines to give a compound which when added to oils in fractional percentages imparts improved stability characteristics and anti-corrosive properties.[21] Examples of these compounds include those formed from salicylic acid and boric acid with either triethanolamine or hexadecylamine.[21] The relationship between the —NH_2 and —OH positions in commercially available anthraquinone base dyes has been determined by using absorption spectral techniques after reaction with boric acid. The constitutions of various boric acid complexes are suggested.[22] The boric acid–salicyloxime–water system has been studied spectrophotometrically[23] and the boric acid *p*-aminosalicylate reaction, which gives a 1:1 complex, was studied by thermal and conductivity measurements.[24]

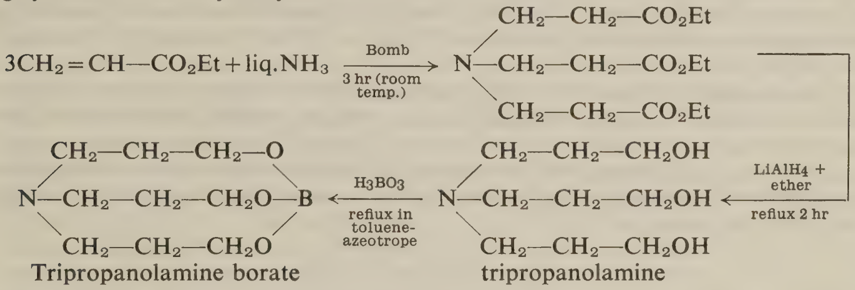
2. Alkanolamine Borates

Alkanolamine borates, despite their name, are strictly esters of boric acid. They are occasionally known as boratranes.[11,42] They are readily prepared, as typified by triethanolamine borates, by the dehydration reaction:

$$N(CH_2CH_2OH)_3 + H_3BO_3 \longrightarrow N(CH_2CH_2O)_3B + 3H_2O,$$

by simple heating[17] or by heating in a variety of organic solvents.[11, 28, 37] For example, boratran, or 2,2′,2″-nitriloethyl borate, is obtained in 90% yield by refluxing equimolar amounts of boric acid and triethanolamine in *iso*-amyl alcohol for 1½–2 hr.[11] Tri-*iso*propanolamine borate may be prepared similarly.[37] Both compounds are white solids, triethanolamine borate melting at 153–156°C (mixture of stereoisomers) and subliming at 135°C/0·19 mm; tri-*iso*propanolamine melts at 235·5–238·5°C, and sublimes at 175°C/0·19 mm.[25, 26] Each is soluble in water (with good hydrolytic resistance; see below), acetone and chloroform, but less so in benzene. They are available commercially[25, 26], and their chemistry has been well reviewed.[37] Because of the tendency of ethanolamine salts to yellow and the consequent disadvantage of using them in the soap industry, a method of producing white salts by treating the amine with sulphur dioxide before the reaction with boric acid (or other acids) was patented.[29]

Tripropanolamine borate is less well-known but has been prepared by an interesting synthesis from ethyl acrylate[32]:



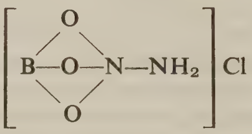
The compound is highly resistant to hydrolysis and has a melting point of 248°C. It was patented for use as a plasticizer for polyacrylonitrile and its copolymers with vinyl acetate, methyl acrylate, acrylamide, styrene, etc.[32]

Whilst considering the formation of these compounds it is perhaps appropriate to consider other amino-esters of boric acid: tris-(2-aminoethyl) borate, $B(OCH_2CH_2NH_2)_3$ and the analogous *N*-methylamino and *N*,*N*-dimethylamino derivatives.[30, 31] These are prepared by trans-esterification of methyl borate with the appropriate 2-aminoethanol. Infra-red and N.M.R. studies have shown that extreme association of the terminal amino groups occurs in pure tris-(aminoethyl) borates. Heating to 160°C or dissolution in polar organic solvents breaks the associative bonds, which appear to be predominantly intermolecular hydrogen bonds.

Tri-*iso*propanolamine borate, like the tri-propanolamine borate, has a high resistance to hydrolysis.[28, 33] Both ethanolamine and *iso*propanolamine are more resistant than the corresponding ethyl and *iso*-propyl borates.[28] These latter esters are straight-chain structures open to easy attack, whereas the alkanolamine borates have a ‘cage’ structure with strong evidence for transannular interaction of amine nitrogen and boron atoms across the eight-membered ring. It is suggested therefore that the boron atom is less available for coordination with water molecules and therefore less likely to hydrolyze, viz.

Although triethanolamine borate is influenced by this structure, it rapidly hydrolyzes at a rate $4{\cdot}11 \times 10^5$ times faster than the tri-*iso*propylamine borate (half life 618 days at 25°C). In addition to the two structures above, commercial tri-*iso*propanolamine borate contains two diastereomers differing in their configuration about one methyl-bearing carbon atom, and influencing the degree of trans-annular association and thus the rate of hydrolysis.[33] The rate of hydrolysis of triethanolamine borate, although fairly rapid (half life = 130 sec), can be increased greatly by sodium tetraphenylboron at pH 6 (acetic acid).[36] This increase in rate of hydrolysis applied to other tri-*n*-alkanolamines which are resistant to hydrolysis. Further work on the structure of triethanolamine borate has been carried out by studies of heat capacities and various thermodynamic functions at 5–350 K.[34] A study of the dielectric constants of the latter borate over the range 283–511 K showed a small change at 474 K. The results of this work confirmed other work that indicated that the material is not plastically crystalline.[35] The crystal structure of triethanolamine borate was determined recently.[42] The length of the coordinate $B \leftarrow N$ bond (structure II) was found to be 1·65 Å, compared with the normal B—N bond length of 1·58 Å. Lattice parameters were determined as $a = 11{\cdot}40 \pm 0{\cdot}05$, $b = 6{\cdot}58 \pm 0{\cdot}01$ and $c = 9{\cdot}71 \pm 0{\cdot}02$ Å; $d(\text{exptl.}) = 1{\cdot}43$.

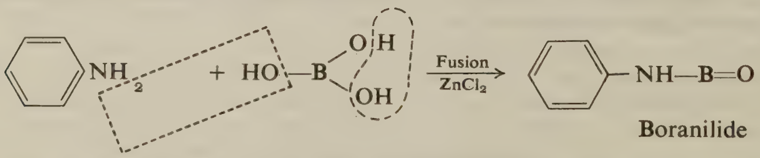
Triethanolamine borate has been suggested as an additive to various polymer reaction mixtures. It gives increased density of linear polyamide crystals for injection moulding by increasing the rate of crystallization[38] and acts as a curing agent for glycidyl polyether resins for the production of electrical insulation for germanium diodes.[39] Modification of triethanolamine borate by reaction with chloramine produces the compound:



which has been used as an epoxy resin curing agent.[40] Triethanolamine borate formed *in situ* to which various other agents are added gives a thixotropic gel with anti-rust, bacteriostatic and fungistatic properties for use as a stable aqueous cutting liquid.[27] It has been previously mentioned that the tri-propanolamine borate has been used as a plasticizer for various acrylic polymers.[32] The addition of small percentages of tri-*iso*propanolamine borate is also valuable in the field of plastics to make co-polymers of acrylonitrile and vinylidene chloride more easily dyeable.[41]

3. Boranilide

Aniline reacts with boric acid in the presence of zinc chloride at 135–140°C to form the so-called boranilide after extraction with water or very dilute acid and recrystallization from alcohol.[43] The reaction involves the elimination of two molecules of water.



Boranilide

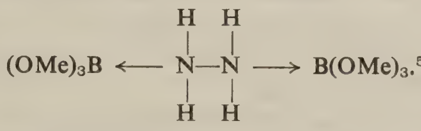
A hydrochloride (m.p. 108–110°C) and a chloroplatinate are known; it forms a benzoyl derivative (m.p. 166°C) by reaction with benzoyl chloride in acetic acid. On heating boranilide with sulphur for 10 minutes, it is transformed into thioboranilide (m.p. 109–110°C). Nitrosoanilide (m.p. 83°C) is formed by its reaction with sodium nitrite in excess hydrochloric acid. Various other derivatives are described and their preparation dealt with in detail.[43]

Reactions of boric acid with certain ion-exchange resins of the amine type are worth mentioning in this context, having some use in the borate industry. The capacity of trimethylammonium type (strong-base) resins varies considerably with the concentration H_3BO_3, probably owing to the penetration of boric acid and the formation of a series of polyborate amines fixed by the resin.[44] Selective adsorption of boric acid occurs on ion-exchange resins prepared with *N*-methyl glucosamine groups[45] and specifically from resins formed from 1-deoxy-1-(methyl amino)-D-glucitol.[46]

4. Hydrazine Borates

Little research on hydrazine borate has been published since Dschawachoff's paper of 1902 in which he described the preparation and properties of $(N_2H_4)_2,(H_2B_4O_7)_3,10H_2O$ and its pentahydrate and anhydrous derivatives.[49] With the formula written in the standard oxide form, this compound is a 1:3-borate, $(N_2H_5)_2O,3B_2O_3,12H_2O$. There appear to be only two other references to similar borates; the 1:2 compound is prepared by reacting equi-molar amounts of hydrazine and boric acid[47], and the hexahydrated 1:3 compound is prepared from one mole of hydrazine and six moles of boric acid.[50] The latter may be purified by recrystallization from water; heating to elevated temperatures (250°C) under slight vacuum converts it to the anhydrous form.[50] The 1:2 compound was found to show herbicidal activity and was patented as a defoliant[47], while the 1:3 compound has been patented as a soldering flux.[50]

Hydrazine reacts with borate esters to form addition compounds in an analogous fashion to ethylene diamine, as described earlier.[5] It is suggested that hydrazine is a stronger ligand than ethylenediamine, as it was possible to form $B(OEt)_2(OMe),N_2H_4$, whereas ethylenediamine would not form an analogous product. Other compounds formed were $B(OEt)(OMe)_2,N_2H_4$ and $B(OPr^i)(OMe)_2,N_2H_4$ and the simple $B(OMe)_3,N_2H_4$ having the structure:



$$\mathrm{(OMe)_3B} \longleftarrow \overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}}\!-\!\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}} \longrightarrow \mathrm{B(OMe)_3}.$$[5]

Further work on the reaction of hydrazine with boron alkoxides and boric acid and the structures of the products has been reported.[48] One alkoxide group of triethyl borate and two alkoxide groups of tri-*iso*-propyl borate are replaced by hydrazino groups at room temperature and 1 mm Hg pressure. Reaction products formed with boric acid are $B(OH)_2N_2H_3,B_2(OH)_2N_2$ and $B(OH)N_2H_2$. It was thought that the products might be polymeric.[48] Addition compounds of hydrazine with triethyl and tri-allyl borates have been prepared and the ^{11}B N.M.R. chemical shift was shown to depend on reactant concentration, which indicates that exchange occurs.[18]

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SECTION A17

ESTERS OF BORIC ACID

BY D. B. GREEN

Boric acid forms esters with alcohols, both monohydric and polyhydric, and the literature on the subject is extensive. It has been reviewed recently by Steinberg et al.[1–4] Nomenclature is often confusing, and that recommended by the American Chemical Society is largely employed in the present text. The simple esters of orthoboric acid, $(RO)_3B$, are variously referred to as borate esters, trialkylborates or trialkoxyboranes; similarly, the cyclic derivatives of metaboric acid, $(ROBO)_3$, are known either as metaborates or, more explicitly, trialkoxyboroxines. The essential feature of all is the B–O–C linkage.

A. GENERAL PREPARATIVE METHODS

Methods of preparation are similar throughout the class. Methods 1 to 6 refer especially to symmetrical orthoborates of monohydric alcohols and phenols, but the general principles can often be applied to the preparation of other boron esters.

1. Interaction of Boric Acid or Boric Oxide with a Monohydric Alcohol

$$3ROH + B(OH)_3 \rightleftharpoons (RO)_3B + 3H_2O$$
$$3ROH + B_2O_3 \rightleftharpoons (RO)_3B + H_2O$$

This is an equilibrium reaction, and the equilibrium lies well over to the left. To drive the reaction to completion, water must be removed, usually by the addition of a suitable hydrocarbon (benzene or toluene) to form a binary azeotrope. Water is removed from the azeotrope (e.g. in the laboratory by using a Dean and Stark apparatus) and the hydrocarbon is recycled. Other methods include use of excess alcohol to give an alcohol/water azeotrope, and use of a ternary azeotrope of excess alcohol/water/hydrocarbon. The above approach has been used successfully for many alcohols, including unsaturated, alicyclic, aromatic and both unsubstituted and substituted saturated alcohols. It is not generally successful with tertiary alcohols, for which special methods often have to be used. These special methods include transesterification[5–7] (see 3 below) and alcoholysis of sodium borohydride:

$$NaBH_4 + H^+ \longrightarrow Na^+ + H_2 + [BH_3]$$
$$2ROH + [BH_3] \longrightarrow (RO)_2BH + 2H_2$$
$$ROH + (RO)_2BH \longrightarrow (RO)_3B + H_2$$

Trimethoxyborane is difficult to prepare in a pure state by the esterification of boric acid, since it forms a low-boiling azeotrope with methanol. Usually, therefore, the azeotrope is initially prepared by interaction of boric oxide and methanol[8] and then broken by one of a variety of methods. This ester is used industrially (see below) and therefore some of the extraction methods will be described. Schiff[9] first separated a mixture of trimethoxyborane and methanol by shaking it with either calcium chloride or concentrated sulphuric acid. These methods give two layers, and the upper layer is considerably enriched in methyl borate. The upper layer can then either be recycled for further enrichment or distilled to give a forerun of the azeotrope, followed by the pure ester. A better yield, and probably also a purer product, was obtained by later workers using lithium chloride.[10] Another method has been to extract the ester with a suitable hydrocarbon[11], though this method must be operated as a continuous cyclic process to be practicable. All these methods are improved by converting them, with modifications where necessary, to a countercurrent extraction process. Other methods used for breaking the azeotrope include addition of a third component to remove the methanol as a lower-boiling ester[10], addition of boric oxide to produce an ester/boric acid mixture, and removal of the methanol by absorption on a molecular sieve.[12]

2. Alcoholysis of Borax or other Alkali Metal Borates in either Neutral or Acidic Media

Methanolysis of borax followed by hydrolysis of the azeotrope has been patented as a method of obtaining boric acid from borax without the use of a strong mineral acid.[13]

$$Na_2B_4O_7 + 6ROH \longrightarrow 2(RO)_3B + Na_2B_2O_4 + 3H_2O$$

Other more obvious methods involve treatment of a sodium or calcium borate with a strong mineral acid and methanol[14]:

$$Na_2B_4O_7 + H_2SO_4 + 16CH_3OH \longrightarrow 4(CH_3O)_3B + 4CH_3OH + Na_2SO_4 + 7H_2O$$

Various other methods of preparing borates from alkali–metal borates have been described and some of them have been patented. They include the novel method of interaction of either borax or colemanite (calcium borate) with carbon dioxide in methanol.[15,16]

3. Transesterification

$$(RO)_3B + 3R'OH \rightleftharpoons (R'O)_3B + 3ROH$$

In essence, this is a simple method of preparation requiring no removal of water. An ester of lower molecular weight (frequently trimethyl borate) is converted into a higher one by treatment with a higher-boiling alcohol. The equilibrium is shifted completely over to the right by distilling off the lower-boiling alcohol. It is possible to prepare a lower-boiling ester from a higher-boiling one under suitable conditions, but the yield is poor. The merit of this reaction is that it can be applied to prepare a wide variety of borates[17] both simple and substituted (e.g. aminoalcohol borates), many of which would not otherwise be easily accessible. The method has been used successfully to prepare a number of tertiary alkyl borates[7,18], which are not easy to prepare: other methods of preparation frequently result in decomposition to alkenes and other products. An interesting potential industrial application for this reaction is the separation of C_7–C_{30} alcohols from hydrocarbons by transesterification with trimethoxyborane followed by distillation.[19] Regeneration of the alcohols is effected readily by a second transesterification with methanol.

A related reaction which can also be considered under this heading is the interaction of triacetoxyborane (see below) with alcohols or phenols[20,21]:

$$(AcO)_3B + 3ROH \longrightarrow (RO)_3B + 3AcOH$$

A problem with this reaction is that special conditions must be used to prevent the acetic acid produced reacting with the borate ester to give boric acid and the acetic acid ester. This is not a common preparative method and other methods are usually preferable.

4. Interaction of Boron Trihalides with Oxygen-Containing Organic Compounds

Suitable compounds include alcohols, phenols, alkoxides, aldehydes, ethers and esters of carboxylic acid. Boron trihalides, particularly boron trichloride, react virtually irreversibly at room temperature with many primary and secondary alcohols and phenols in stepwise reactions to give trialkoxyboranes.[22]

$$BCl_3 + 3ROH \longrightarrow (RO)_3B + 3HCl$$

This is a parallel to the reaction of acyl halides with alcohols to form carboxylic acid esters. The simplicity of this reaction, which can frequently be performed at or below room temperature, is clearly advantageous for the preparation of many esters and especially substituted aromatic borates. The reaction can be used to prepare tertiary alkoxyboranes, which are sensitive to hydrogen chloride, by adding pyridine to the mixture.[23] The treatment of various complexes of boron trichloride with the alcohol has also been used to prepare alkoxyboranes. These include ether, tetrahydrofuran, dioxane, triphenyl phosphate and acetonitrile complexes.

Boron tribromide reacts in a similar way to the trichloride in many cases but it has a stronger tendency to halogenate the alkyl group of the alcohol.[24] Boron trifluoride has a very different reactivity and the reaction often gives a complex and sometimes dehydrates the alcohol to the olefin, which may polymerize in the presence of the trifluoride. It is possible to produce certain alkoxyboranes using a boron trifluoride–alcohol complex or by adding a suitable base such as urea. Boron tri-iodide has not been reported to produce an alkoxyborane. Sodium[25] or aluminium[26] alkoxides react readily with either boron trichloride or trifluoride to give the alkoxyborane:

$$3EtONa + BCl_3/BF_3 \longrightarrow (EtO)_3B + 3NaCl/3NaF$$

Ethers have been shown to react stepwise with boron trichloride[27] to yield dialkoxychloroboranes which, although they did not react further with the ether, disproportionated or reacted with the monoalkoxydihaloborane as shown below:

$$\begin{aligned} 2(RO)_2BCl &\longrightarrow ROBCl_2 + (RO)_3B \\ (RO)_2BCl + ROBCl_2 &\longrightarrow BCl_3 + (RO)_3B \end{aligned}$$

Borate esters have also been obtained in good yield from the reaction of boron tribromide with ethers[28], and from boron trifluoride etherate by interaction with certain amine hydrochlorides.[29]

$$\begin{aligned} 3RNH_3Cl + 3Et_2O{:}BF_3 \xrightarrow{60-100°C} \; & 3EtCl + RNH_3[EtOBF_3] \\ & \qquad\qquad \downarrow \\ & (EtO)_3B + 2RNH_3[BF_4] + RNH_3F \end{aligned}$$

Trialkoxyboranes have also been formed from the reaction of boron trichloride with cyclic ethers, aldehydes (providing the only direct path to α-chloro esters), carboxylic esters, phosphorus and silicon esters and several less common oxygenated compounds. Boron tribromide can also be used in some of these reactions. Many of the reactions are complex, and for further information the reader is referred to two well-known reference works on the subject.[1,3]

5. Disproportionation, Decomposition or Reaction of Alkoxyhaloboranes

Disproportionation and decomposition were briefly discussed under 4 above. Although trialkoxyboranes can be prepared by the reaction of alkoxyhaloboranes (with, for example, an alcohol or carboxylic acid), there is usually no advantage in the method since both the dialkoxyhaloboranes and the alkoxydihaloboranes are normally and most conveniently made from the boron trihalide and the alcohol/phenol or alkoxide/phenoxide. In special cases the method can offer advantages and the reader is referred to a more comprehensive study for details.[1] The alkoxyhaloboranes are essentially intermediates in the reaction of boron trihalides with alcohols. Their thermal stability is very variable, but in general they are much less stable than the trialkoxyboranes.

6. Other General Methods

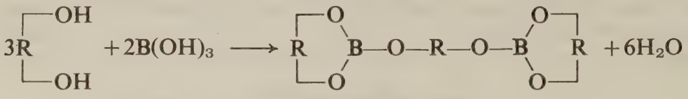
There are many other reactions which lead to the formation of trialkoxyboranes, but few would be used for their preparation except in special cases: for example, the thermal decomposition of trialkoxyboroxines or their reaction with alcohol. Trialkoxyboroxines are usually prepared from the borate ester and boric oxide.[30, 31] Alcoholysis of alkali–metal borohydrides is sometimes useful and of particular note is the preparation of tri-*tert*-alkoxyboranes by the alcoholysis of sodium borohydride (see 1).

7. Reactions of Boric Acid/Oxide or Boron Trichloride with Polyhydric Alcohols and Phenols

The interaction of boric acid/oxide or boron trichloride with a polyhydric alcohol or phenol can lead to a variety of products depending upon the stoichiometry and conditions of the reaction.

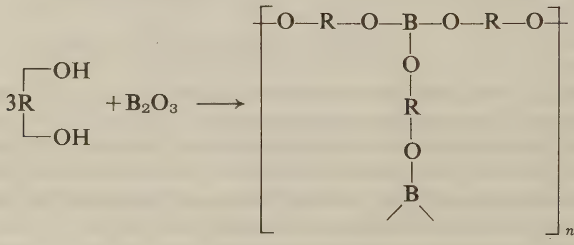
(a). Glycol Biborates

These may be prepared by basic methods given in 1, 3 and 4 (above) by using suitable stoichiometric quantities of boron source and glycol. For example, by the method in 1, the interaction of two moles of boric acid (or 1 mole of the anhydride) with at least 3 moles of a diol gives a glycol biborate:



The water is removed by azeotrope formation or even by heating under slightly reduced pressure.[32, 33] Similarly the method in 4 can be used (boron trichloride and glycol) and this can give excellent yields of biborates.[34]

1,2- and 1,3-glycols usually give monomeric products, but 1,4- and higher glycols usually give a polymeric product:



If the stoichiometry is changed and less than 3 moles of glycol are used per 2 moles of boric acid, even 1,2-glycols such as ethylene glycol are said to give polymeric products.[35]

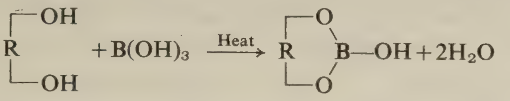
(b). 2-Hydroxy-1,3,2- dioxaborolanes and borinanes and related compounds

(i). HYDROXYBORESTERS OF MONOHYDRIC ALCOHOLS

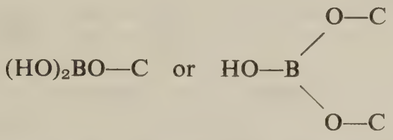
Dialkoxyhydroxyboranes, $(RO)_2BOH$, do not exist, except perhaps as intermediates in esterification reactions. One or two examples of alkoxydihydroxyboranes have been prepared from sterically hindered monohydric alcohols or phenols.[36] Thus the chemistry of hydroxyesters of monohydric alcohols is very limited.

(ii). HYDROXYBOROLANES AND BORINANES

The chemistry of these special esters of boric acid is dominated by the reaction products of glycols with boric acid, i.e. preparation by the method in A, 1 (above).



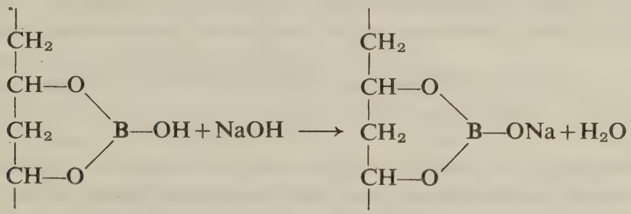
Certain polyhydric alcohols and phenols have also been reported to give various compounds containing the



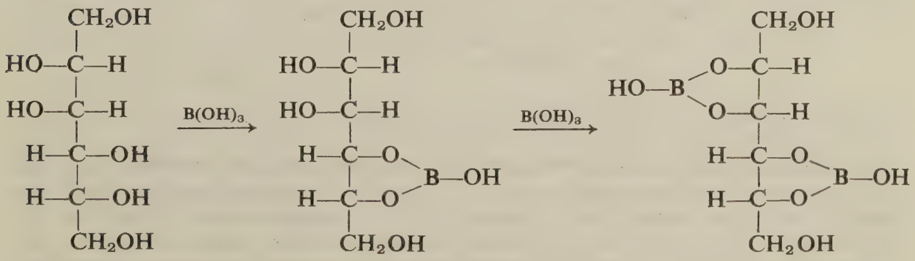
groupings

1,2- and 1,3- glycols react with an equimolar quantity of boric acid to give the hydroxyborolane (5-membered ring) or borinane (6-membered ring). This reaction is very simple and occurs so readily in some cases that equimolar quantities of the reactants may be simply dissolved in hot water and the product isolated by subsequent cooling and filtration.[37] This facile reaction distinguishes these esters from the esters of monohydric alcohols, where the esterification rate is slow in non-aqueous solvents and the products are all readily hydrolysable. The reaction does not always proceed rapidly and notable exceptions are ethylene and propylene-1,3-glycols.[37] The higher glycols do not yield an isolatable hydroxyester.

Polyvinyl alcohol reacts with an aqueous solution of boric acid to give a white solid.[38] This solid reacts with sodium hydroxide to give a salt, and for this reason the product is believed to contain borinane rings.



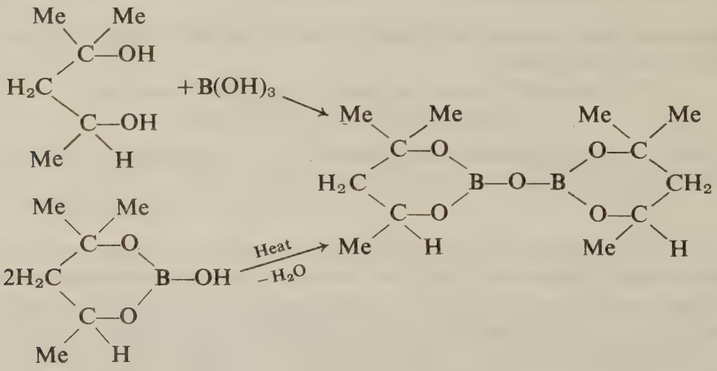
Sugar alcohols, such as mannitol, react with boric acid either by direct heating of an equimolar mixture or by making an aqueous solution of the mixture to form products containing a borolane ring. Using a 1:2 mole ratio of sugar to boric acid results in a bisborate by esterification of the remaining two hydroxy groups.[39]



Borolanes and borinanes may be prepared by several other methods, but in practice these usually involve a two-stage reaction and the methods already described may therefore be regarded as by the far the most common.

(iii). 2,2′-OXYBIS-(1,3,2-DIOXABOROLANES AND BORINANES)

These anhydrides of the 2-hydroxyborolanes and borinanes are usually prepared by azeotropic distillation of a 1:1 molar mixture of boric acid and the 1,2- or 1,3-glycol.[40] Suitable molar ratios of boric oxide or metaboric acid and the glycol may also be used in a similar manner. Another method of preparation is to dehydrate the corresponding hydroxyborolane or borinane, which loses water readily on heating.[41, 42]



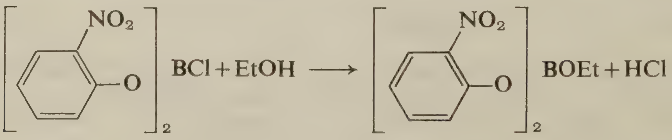
8. Preparative Methods for Classes of Compounds Not Specifically Mentioned in 1 to 7

(a). Unsymmetrical Orthoborates

Most of the simple unsymmetrical or mixed orthoborates of either aliphatic or aromatic or mixed alcohols undergo disproportionation reactions so readily that they virtually do not exist at room temperature. Attempts to isolate them from reactions such as that shown below result only in the isolation of the symmetrical orthoborates:

$$(EtO)_3B + n\text{-}BuOH \longrightarrow [(EtO)_2BOBu] + EtOH$$
$$\downarrow$$
$$(EtO)_3B + (BuO)_3B$$

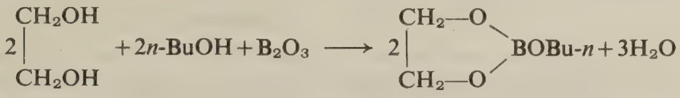
However, two types of relatively simple mixed orthoborates do exist. These are those derived from *o*-nitrophenol and from 2,6-di-*t*-alkylphenols. The stability of these two types of mixed ester may be due to steric factors. The latter type is sufficiently stable to be distilled under reduced pressure and is also exceptionally stable to hydrolysis. Its hydrolytic stability may also be attributable to donation of π electrons from the ring to the boron atom. Bis-*o*-nitrophenoxyethoxyborane was prepared by treating the chloroborane with ethanol[43]:



The *bis*-alkoxy-2,6-di-*t*-alkylphenoxyboranes have been prepared similarly from the dichloroborane, by transesterification of a trialkoxyborane with the phenol replacing one of the simple alkoxy groups with a di-*t*-alkylphenoxy group and by esterification of a 2-hydroxy-1,3,2-dioxaborinane. Simple transesterification has also been used to replace the two alkoxy groups with a glycol to give a dioxaborinane. Much of this work has been done by Steinberg and his co-workers.[44]

It has been reported[45] that unsymmetrical glycol biborates can be prepared from a mixture of 1,3- and 1,4-glycols with boric acid in a similar way to the symmetrical biborates (see 7(a) above). The formation of mixed products is virtually eliminated as 1,4-glycols do not readily form a ring.

2-Alkoxy/phenoxy-1,3,2-dioxaborolanes and borinanes are usually simply prepared by using a method analogous to that for orthoborates (see 1 above) except that 2 moles of monohydric alcohol are replaced with one of diol[46]:



These esters are relatively much more thermally stable than the mixed esters of the monohydric alcohols, which is probably attributable to the stability of the five-membered ring. There are various other preparative methods but these are all more complex and are of value mainly for the preparation of compounds which for one reason or another are not readily prepared by the method just described. The most important of these are the esterification of 2-hydroxy-1,3,2-dioxaborolanes and borinanes[47] or of the 2-chloro derivative[48,49], the transesterification of 2-alkoxy-1,3,2-dioxaborolanes with a monohydric alcohol or of a trialkoxyborane with a dihydric alcohol[50]; the interaction of trialkoxyboranes and glycol biborates[51]; and the alcoholysis of 2,2′-oxybis-(1,3,2-dioxaborolanes).[42]

(b). Mixed Anhydrides of Boric Acid and Carboxylic Acids

By far the best known compound in this class is acetyl borate. In the literature both triacetoxyborane (A) and tetra-acetoxy diborate (B) are described. There is

$$(CH_3CO_2)_3B \qquad\qquad (CH_3CO_2)_2B{-}O{-}B(O_2CCH_3)_2$$

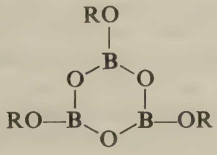
A. B.

no doubt that the diborate exists, but there is considerable controversy about the triacetoxy compound, which appears at least to be very difficult to prepare. In the author's own experience, all attempts to prepare the triacetoxy compound have failed. However, several workers have reported the isolation of this compound, and a possible explanation is that it readily undergoes an intermolecular elimination reaction losing acetic anhydride to give the diborate.

The diborate may be prepared by the interaction of acetic anhydride with boric acid, boric oxide, metaboric acid, boron trichloride and trialkoxyboranes. Workers reporting the triacetoxy compound have used the reaction of at least 3 moles of acetic anhydride with either boric acid or boric oxide.[21] Both products have also been claimed to be formed by the interaction of acetyl chloride with boric acid, and the tricarboxyboranes of other acids including benzoic[21] and cinnamic[52] are reported to have been prepared by this method from the corresponding acid chlorides. Either the diborates or the tricarboxyboranes of a number of carboxylic acids may also be prepared by the interaction of the carboxylic acid with boron trichloride or tribromide, an alkoxychloroborane, diborane or a trialkylborane. Rather like the transesterification of orthoborate esters, higher mixed anhydrides of boric acid can be prepared by the interaction of tetra-acetoxy diborate (or the *in situ* product of acetic anhydride and boric acid) with a higher carboxylic acid.

(c). Trialkoxyboroxines

Trialkoxyboroxines are essentially esters of metaboric acid. The stoichiometric formula of metaboric acid is HO—B=O, but in fact this compound is generally accepted to be polymeric and its esters are trimeric rings (see below) and are therefore termed trialkoxyboroxines.



Only the primary and secondary alkoxyboroxines have been reported. They are usually viscous liquids, but a few crystalline compounds are also known.

There are a number of common methods for preparing alkoxyboroxines but in the author's view the laboratory method of choice (and also the method giving the purest products) in most cases is the interaction of boric oxide with an orthoborate ester.[30]

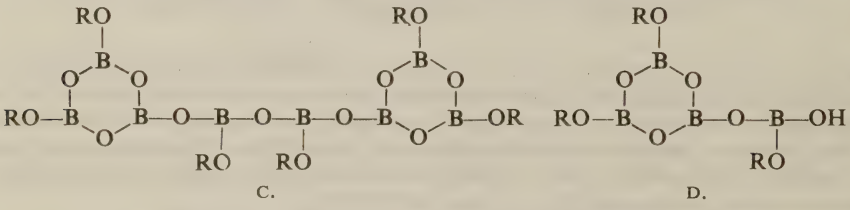
$$(RO)_3B + B_2O_3 \longrightarrow (ROBO)_3$$

The reaction is usually very slow but can be considerably accelerated by using boric oxide having a high surface area (prepared by gentle heating of boric acid under vacuum) and adding a trace of an alcohol (usually the one which would result from the hydrolysis of the orthoborate ester). Other methods include: interaction of either boric acid, metaboric acid or boric oxide with the stoichiometric quantity of an alcohol and removal of the water by azeotrope formation, heating or simply use of reduced pressure (see 1, above); and decomposition of a dialkoxyhaloborane either thermally or catalytically with a Lewis acid.

$$3(RO)_2BCl \longrightarrow (ROBO)_3 + 3RCl$$

Transesterification of a simple alkoxyboroxine with a hindered phenol has also resulted in the formation of a boroxine.

Polyborates are known as well as boroxines. These are simply compounds where the ratio of boron atoms to alkoxy groups is greater than one. Clearly this is a very large class of compounds, but certain well-defined members, mainly those having a 4:3 ratio of boron to alkoxyl groups (C and D), are clearly defined. These compounds are usually prepared by one of two methods both analogous to those used for the boroxines. These are interaction of the alcohol with boric/metaboric acid or anhydride[36] and reaction of an orthoborate with boric oxide.[53]



(d). Peroxyboranes

Peroxyboranes can be regarded as alkyl- or acyl-oxyboranes with an extra oxygen between the boron atom and the alkoxy group. The following structures have been reported:

$(ROO)_3B$	$(ROO)_2BOH$	$(ROO)_2BOR'$	$ROOB(OR)_2$
I.	II.	III.	IV.

Methods of preparation by the interaction of a hydroperoxide with a trialkoxyborane are discussed under reactions of the B—OR group under 7(g) (p. 717). Nucleophilic substitution can also be done with boron trichloride and alkyl hydroperoxides[54]:

$$BCl_3 + 3Bu^tOOH \longrightarrow B(OOBu^t)_3 + 3HCl$$

An alternative method of preparation is by the autoxidation of trialkylboranes.[55, 56] This method may be used for peroxyboranes having structures (III) and (IV).

$$R_3B \xrightarrow{O_2} R_2BOOR \xrightarrow{O_2} RB(OOR)_2$$

Treatment of alkyldialkylperoxyboranes with pyridine, piperidine or water leads to rearrangement to give the dialkoxyalkylperoxyboranes. Trialkylperoxyboranes are readily and completely hydrolysed and also undergo alcoholysis very easily.[54]

$$(ROO)_3B + 3H_2O \longrightarrow H_3BO_3 + 3ROOH$$
$$(Bu^tOO)_3 + 3EtOH \longrightarrow 3Bu^tOOH + (EtO)_3B$$

Tri-*t*-butylperoxyborane (but not *n*-butyl) forms rather unstable insoluble 1:1 complexes with some amines.[54] Trialkylperoxyboranes react with alkenes to give epoxides in good yield.[56] It has also been claimed[57] that they will react with aromatic hydrocarbons to give phenols, but the author was not able to verify this reaction.[58] Both tri-*n*-butyl and tri-*t*-butylperoxyboranes have been shown to catalyse the polymerization of styrene and methyl methacrylate.[54, 59] This is good evidence for the homolytic fission of the O–O bonds.

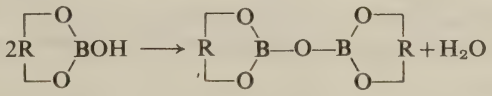
B. REACTIONS OF THE B—OR GROUP

1. Thermal Stability

The symmetrical orthoborate esters except for the tertiary alkyl esters are generally very stable thermally. There are many references to the thermal decomposition of orthoborates to give alkenes. However, except for the tertiary alkyl borates and many higher molecular-weight borates, it is generally not the orthoborate but in effect the metaborate which has been pyrolysed to give the alkene. Mixtures of secondary and tertiary alcohols can be separated by conversion into the borate esters[60] followed by high-temperature distillation, when the tertiary alkyl borates are pyrolysed to eliminate the corresponding olefin. The aromatic orthoborates are particularly stable and their increased stability is probably due to the stronger C–O bond and also the free-radical-stopping properties of the phenyl group.

The pyrolysis of various alcohol/boric acid mixtures has resulted in the formation of alkenes. The proportions of the reactants suggest that the reaction proceeds through the metaborate. There is evidence that the reaction is acid-catalysed and proceeds through a carbonium ion mechanism.[61]

The thermal stability of orthoborates of dihydric alcohols and phenols has been very little studied. The action of heat on unsymmetrical orthoborates can cause both decomposition and disproportionation, and frequently (as might be expected) these esters will decompose by either or both routes more readily than most symmetrical orthoborates. 2-Hydroxy-1,3,2-dioxaborolanes and borinanes are readily dehydrated on heating to give the anhydride, but the anhydride itself is thermally very stable, at least when R is aryl.[42]



Tetra-acetoxy diborate is decomposed at about 150°C to give acetic anhydride and a residue whose analysis suggests it is *tris*acetoxyboroxine.[62] Limited data available on diacyloxyaryloxyboranes show a similar reaction to give acetic anhydride and the metaborate (boroxine). Thermolysis of triacetoxyborane is discussed under 8(b), above.

2. Hydrolytic Stability

In general the B–OR bond is readily hydrolysed. However, bulky alkyl or aryl groups giving steric hindrance and suitable electronic factors render certain borate esters remarkably stable. Most of the symmetrical orthoborate esters are hydrolytically very unstable.

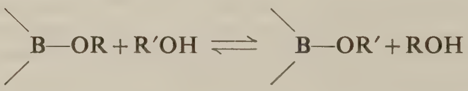
$$(RO)_3B + 3H_2O \rightleftharpoons 3ROH + B(OH)_3$$

As might be expected, the secondary and tertiary alkyl esters are generally more stable than the primary ones. Glycol biborates are readily hydrolysed to boric acid and the glycol although a partially hydrolysed product, the 2-hydroxy-1,3,2-dioxaborinane, can be isolated under certain conditions. Unsymmetrical orthoborates are also generally unstable to hydrolysis, with a few exceptions including the hindered phenolic borates.[63]

Like most other borate esters, the boroxines are generally rapidly hydrolysed. The size of the alkyl group has little effect on the speed of hydrolysis, owing to the separation of the three groups by the ring structure. Hindered phenolic boroxines are more slowly hydrolysed, and it is sometimes possible to isolate the intermediate dihydroxyaryloxyborane, which is precipitated from water.[63] Trialkanolamine borates are only very slowly hydrolysed.[63] This is probably due to the stable triple-ring structure and to an increase of electron density on the boron atom resulting from nitrogen coordination. Tri-*n*-propanolamine borate is exceptionally stable and may well be the most stable borate ester known.[64]

3. Alcoholysis

The reaction of orthoborates and acetoxyboranes with alcohols and phenols has already been discussed under 3, above. This reaction is very important with all the borate esters, because, except where inhibiting steric and electronic factors are involved, the B–OR bond is very labile. In any alcohol/borate mixture there is nearly always an equilibrium of the following type:



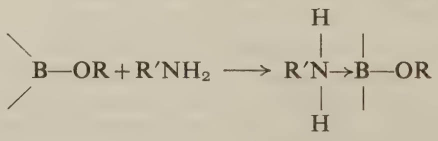
$$>B\text{—}OR + R'OH \rightleftharpoons >B\text{—}OR' + ROH$$

In transesterification the equilibrium is eventually moved completely to one side by distilling off the lower-boiling alcohol. The principle can be used for the preparation of 2-alkoxy-1,3,2-dioxaborolanes. The reverse procedure is used in the analysis of high-boiling glycol borates when methanol in excess of the stoichiometric quantity is added and the methanol/methyl borate azeotrope distilled out.

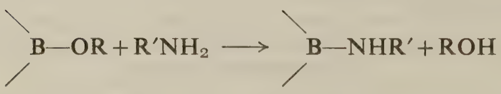
There appears to be no reason why boroxines should not be prepared by alcoholysis and distilling out the lower-boiling alcohol. In practice, fission of the B–O ring occurs and a mixture of the orthoborates and boric acid is obtained.

4. Reaction with Amines

Compounds containing the B–OR bond usually react with amines in one of two ways: (a) complex formation; (b) displacement of an alkoxy group by an alkylamine group:



$$>B\text{—}OR + R'NH_2 \longrightarrow R'\overset{H}{\underset{H}{N}}\rightarrow B\text{—}OR \qquad (a)$$



$$>B\text{—}OR + R'NH_2 \longrightarrow >B\text{—}NHR' + ROH \qquad (b)$$

(a). Complex Formation

Boron trichloride reacts readily with most amines to give a complex, but in the borate esters the electron density is increased on the boron atom by the inductive effect of the alkoxy group. For this reason trimethoxyborane is the only simple aliphatic borate ester which forms complexes. This is because both the $+I$ effect and the steric effects are at a minimum. Generally, strongly basic amines with no steric hindrance form complexes with trimethoxyborane.[65] In boron esters having chlorinated (or other $-I$) alkyl groups the $+I$ effect is reduced and once again complexes are sometimes formed. However, steric effects can sometimes prevent complex formation even though electronic factors are favourable, e.g. tri-(2,2,2-trichloroethoxy)borane does not form a stable complex with pyridine[66], but replacing the chlorine with fluorine reduces steric strain and a complex has been isolated from this fluorinated borate.[67]

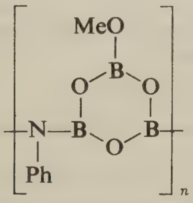
The triaryloxyboranes readily form complexes even with quite weakly basic amines such as pyridine. This is expected because of the reduced electron density on the boron atom resulting from the $-M$ effect of the aromatic ring. The other important factors in determining the course of reaction of the $>$B—OR group with an amine are the basic strength of the amine and whether or not it is sterically hindered. Stronger, more bulky amines such as diethylamine will not form a complex with trimethoxyborane, presumably because of steric factors. In general this is also true with the aromatic boron esters but there are certain exceptions such as the complex of tri-*m*-cresyloxyborane with di-isobutylamine. A 1:1 complex of 2,3-butanediol biborate with benzylamine has been described.[33] Those unsymmetrical orthoborates having an aryloxy group generally form stable 1:1 complexes with certain amines such as pyridine and aniline.[51] As might be expected, the totally aliphatic ones do not complex nearly so readily and when complexes are formed they are unstable.[33]

(b). Displacement Reactions

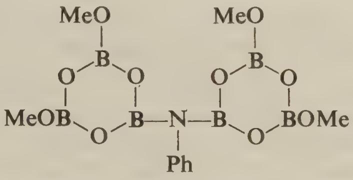
Orthoborate esters can be made to react with primary amines, the alkoxy group being substituted with an alkylamino group:

$$(i\text{-}C_3H_7O)_3B + 3C_6H_{11}NH_2 \longrightarrow (C_6H_{11}NH)_3B + 3i\text{-}C_3H_7OH$$

In many cases the reaction is slow, even under reflux conditions with a high-boiling amine such as aniline.[68] Trimethoxyboroxine is reported to react readily with aniline and substituted anilines[69], and can react to produce either a monomer (B) or a polymeric compound (A) according to the stoichiometry:

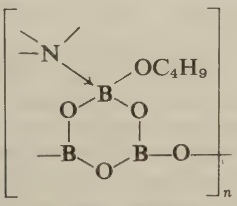


A.



B.

This contrasts with the comparative difficulty of reacting an orthoborate with an amine. Tributoxyboroxine reacts with a number of amines to form a complex formulated as (C):



C.

and tributoxyborane.[70]

5. Reactions with Acids, (a) Carboxylic, (b) Inorganic

(a). Carboxylic Acids

Orthoborate esters usually react with carboxylic acids to give the corresponding carboxylic ester and boric acid:

$$(RO)_3B + 3R'CO_2H \longrightarrow 3R'CO_2R + H_3BO_3$$

This reaction has been used as a simple method for the preparation of acetates, benzoates and cinnamates of primary, secondary and tertiary alcohols and phenols. Boroxines have also been shown to react similarly both with carboxylic acids, anhydrides and chlorides. The interaction of orthoborate esters with acid anhydrides to give the tetra-acyloxy diborate and acyl ester has been mentioned under 8(b), above.

(b). Inorganic Acids

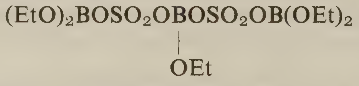
The general reaction of the B–OR bond with an inorganic acid is alkylation of the acid[9]:

$$(EtO)_3B + 3HNO_3 \xrightarrow{\text{Heat}} 3EtONO_2 + B(OH)_3$$

Similar reactions occur with hydrogen bromide and iodide and in certain cases with hydrogen chloride. However, with hydrogen chloride there is sometimes no reaction or it stops short of complete dealkylation[71]:

$$(RO)_3B + 2HCl \longrightarrow 2ROH + ROBCl_2$$

Hydrogen bromide also reacts with tri(ethylene glycol) biborate to give ethylene bromide and boric acid. Phosphoric acid reacts with orthoborates to give ultimately boron phosphate and the alcohols/alkylphosphates.[71] Sulphuric acid reacts in a similar way with triethoxyborane[71,9], except that the intermediate compounds formed are more stable and the reaction stops short of "boron sulphate" (q.v.) to give a residue having the formula:



$$(EtO)_2BOSO_2O\underset{\displaystyle OEt}{\underset{|}{B}}OSO_2OB(OEt)_2$$

The reaction of trialkoxyboranes with hydrogen fluoride does not follow the general pattern and boron trifluoride dialcoholates are formed.[72]

$$(RO)_3B + 3HF \longrightarrow BF_3{,}2ROH + ROH$$

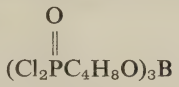
Trimethoxyboroxine also reacts with hydrogen fluoride to give a complex containing boron trifluoride, methanol and water.[72]

6. Reactions with Halogen Compounds and Friedel–Crafts Reaction

There is little in the literature about the reactions of halogen compounds with the B–OR group, except for the reactions of the orthoborates. The exception is the reactions with boron trihalides and the Friedel–Crafts reaction which are discussed below. It has been claimed in a patent that both trimethoxyborane and trimethoxyboroxine react with chlorine to give boron trichloride, phosgene and hydrogen chloride[73]:

$$(MeO)_3B + 9Cl_2 \longrightarrow BCl_3 + 9HCl + 3COCl_2$$

A few other reactions of orthoborates with chlorine have also been described, but the products tend to be complex. Orthoborate esters do not in general react readily with normally reactive halides such as those of Groups III to V, and thionyl and acyl chlorides, but under vigorous conditions or in the presence of ferric chloride they can be made to do so. For example, silicon tetrachloride will not react with boiling tributoxyborane until a small amount of ferric chloride is added, when butene and butyl chloride are evolved and the residue contains boric oxide and silica.[74] Similarly, phosphorus trichloride reacts with tributoxyborane only if either ferric chloride or some oxygen is present.[74] In the presence of oxygen, a thermally unstable phosphorylated product (A) is obtained, but when ferric chloride



$$(Cl_2\overset{\overset{O}{\|}}{P}C_4H_8O)_3B$$

A.

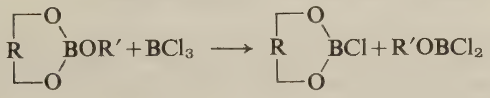
is present, prolonged heating at 95°C results in evolution of butyl chloride. Tributoxy-borane also reacts with thionyl or acetyl chlorides only in the presence of ferric chloride[74], giving respectively sulphur dioxide and butyl chloride, and butyl acetate and chloride. Phosphoryl chloride reacts readily with trialkoxyboranes[75] to form the alkyl halide and boron phosphate.

$$(RO)_3B + POCl_3 \longrightarrow 3RCl + BPO_4$$

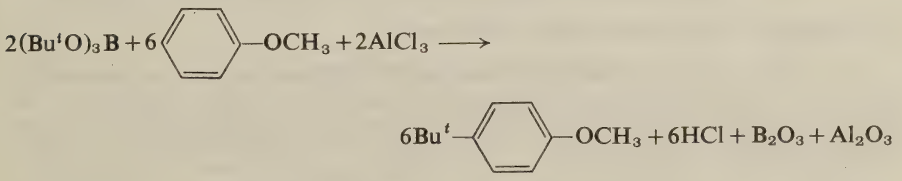
Boron trichloride reacts with orthoborate esters and other compounds having the B–OR bond. Gerrard and his co-workers have reported many of the known reactions of boron trichloride with compounds containing the B–OR group. The reaction with orthoborates is a convenient preparative method for alkoxychloroboranes[76] and a similar reaction also occurs with alkoxyboroxines.[70]

$$2BCl_3 + (RO)_3B \longrightarrow 3ROBCl_2$$
$$3BCl_3 + (BuOBO)_3 \longrightarrow 3BuOBCl_2 + (ClBO)_3$$

Many alkoxydichloroboranes decompose well below room temperature, but a few are stable at 20°C or higher. 2-Alkoxy-1,3,2-dioxaboranes also react similarly:



Symmetrical[77] and unsymmetrical orthoborates, ethylene glycol biborate[78] and triacyloxyboranes[79] have all been used in the Friedel–Crafts reaction:

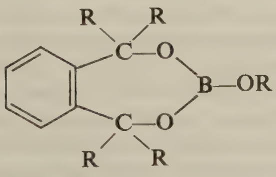


Alkyl group rearrangement follows the normal pattern of the Friedel–Crafts reaction. The Lewis acid most used was aluminium trichloride, but ferric chloride and sulphuric acid were also used in a few reactions. Trialkoxyboroxines do not appear to act as alkylating agents in the Friedel–Crafts reaction.

7. Other Reactions mainly of Orthoborate Esters

(a). Reaction with Metals

Neither tributoxyborane[80] nor trimethoxyborane[81] react with sodium, but unsymmetrical borates of type (A):



A.

are cleaved across either one or both C–O and B–O bonds of the ring to give a mixture.[50]

(b). Reaction with Silanols

Trialkoxyboroxines react with triethylsilanol to give *tris*(triethylsiloxy)borane.[82]

$$(Bu^nO)_3B + 3Et_3SiOH \longrightarrow (Et_3SiO)_3B + 3Bu^nOH$$

(c). Reactions with Metal Hydrides

The reaction of an orthoborate with metal hydrides depends upon the stoichiometry and reaction conditions and the following reactions are all known:

$$\begin{array}{rcl} (RO)_3B + MH & \longrightarrow & [(RO)_3BH]M \\ & & \downarrow \text{ 4 moles of complex} \\ 4(RO)_3B + 4MH & \longrightarrow & MBH_4 + 3MB(OR)_4 \\ 2(RO)_3B + MH & \longrightarrow & (RO)_2BH + MB(OR)_4 \\ (RO)_3B + 4MH & \longrightarrow & MBH_4 + 3MOR \end{array}$$

Trialkoxyboroxines also undergo some similar reactions. For further detail the reader is referred to Steinberg.[83]

(d). Reactions with Boron Hydrides and Trialkylboranes

It has been reported that the lower trialkoxyboranes will react with pentaborane-9 in the presence of aluminium chloride at 100°C.[84] Trialkoxyboranes and trialkylboranes undergo exchange reactions, but only under fairly forcing conditions at high temperatures and pressures.[85]

$$(RO)_3B + R'_3B \longrightarrow (RO)_2BR' + R'_2BOR$$

(e). Reactions with Organometallic Compounds

The reaction of compounds containing the B–OR bond with an organometallic compound is one of the most common methods of forming the B–C bond. The Grignard reagent is probably more used than any other, and either one, two or all three groups can be replaced.

$$\begin{tikzcd} (RO)_3B + R'MgX \arrow[r] & R'B(OR)_2 \arrow[r, "R'MgX"] & R'_2B(OR) \arrow[d, "R'MgX"] \\ & & R'_3B \end{tikzcd}$$

(f). Reduction (see also 7(c)) and Oxidation

The reduction of trimethoxyborane with hydrogen and either aluminium powder and an aluminium chloride–sodium chloride flux at 170°C[86], or by passage through a graphite tube at 1400°C[87], has been reported to give volatile products including diborane. Both trimethoxyborane and trimethoxyboroxine are reported to give diborane using the first method.[86] The reduction of trimethoxyboroxine with lithium aluminium hydride is said to give up to 90% yield of lithium borohydride.[88] Trialkoxy- and especially triaryloxyboranes are very stable towards air oxidation even at high temperatures. Industrial use is made of this property in the air oxidation of hydrocarbons (particularly cyclohexane) in the presence of boric acid.[89] The stability of the orthoborate formed as the main end-product is an important factor in making it possible to obtain a high yield of alcohol (by hydrolysis on completion of the reaction) with a relatively small amount of more highly oxidized by-products and a much higher alcohol:ketone ratio than would otherwise be obtained.

(g). Reaction with Hydroperoxides

Davies and his co-workers[54, 59] first studied the interaction of an alkyl hydroperoxide with a trialkoxyborane:

$$3ROOH+(Pr^nO)_3B \rightleftharpoons (ROO)_3B+3Pr^nOH$$

They attempted to prepare tripinanylperoxyborane by heating tri-*n*-propoxyborane and the hydroperoxide under reduced pressure. A rather impure product was obtained and the method was also unsatisfactory with *t*-butyl hydroperoxide. A similar experiment using cumyl hydroperoxide resulted in an exothermic reaction and the formation of phenol. Rhône–Poulenc[90] later patented a method based on this scheme for the preparation of trialkylperoxyboranes. The difference is that they used trimethoxyborane or at least one of the lowest alkoxyboranes in large excess, the alcohol liberated being removed as the trimethoxyborane/alcohol azeotrope. A further patent[91] specifies the same reactants, but they are passed through a molecular sieve to remove the alcohol as it is formed. Little or no heating is necessary and only a small excess of alkoxyborane is needed.

(h). Reaction with Alkoxides and Hydroxides

All but the tertiary alkyl esters and including triphenoxyborane usually react with metal alkoxides of sodium, lithium and potassium (and others in some cases) to give the metal tetra-alkoxyborate[92]:

$$(Pr^iO)_3B+Pr^iONa \longrightarrow (Pr^iO)_4BNa$$

The reaction is reversible at high temperatures. In this reaction the boron atom goes from sp^2 hybridization (in which state it is electron deficient) to sp^3 (when it is satisfied by donation of an electron pair from an extra oxygen atom). As would be expected the tetra-alkoxy compounds are largely ionic in character, the boron atom formally being given a negative charge. They are readily hydrolysed. Mixed alkoxy-hydroxy tetraborates have been described in the literature.[92, 93]

USES OF BORATE ESTERS

There are a large number of patents on the uses of borate esters. In practice relatively few are worked. The simplest ester, trimethoxyborane, is normally used as a solution in methanol or acetone as a gas flux for welding.[94] Trimethoxyboroxine, usually mixed with another boroxine, is used for the curing of certain types of epoxy resins.[95] Tri-*m,p*-cresoxyborane is also very effective for curing epoxy resins derived from peracid oxidation of olefins.[96] Borate esters, usually glycol biborates, are used as fuel additives to reduce the octane requirements for automobile fuels.[97, 98] They are also used in both automotive and jet fuels as anti-icing agents and microbiocides.[99, 100] Various glycol borates are used as additives to hydraulic fluids, lubricating oils and greases. They are added for several reasons, reduced corrosion[101, 102] and increased resistance to oxidation even at high temperatures[103] probably being the most significant. Recently, there has been considerable interest in the use of the borate esters of glycol monoethers as components of high-boiling hydraulic fluids.[104] Conventional hydraulic fluids eventually break down, partly because of absorption of water, but the hydrolysis products of these borate esters are still relatively high-boiling and therefore these new brake fluids are claimed to be relatively water insensitive.

Metaboric acid is used in the air oxidation of cyclohexane to direct the oxidation towards the production of cyclohexanol.[89] The end product before hydrolysis is in fact tricyclohexoxyborane and in this sense a borate ester does take part in a very important industrial process. A similar process is also used industrially for the preparation of cyclododecanol from cyclododecane.[105] Interest also seems to be growing in the preparation of long-chain secondary alcohols for the manufacture of readily biologically degradable detergents.[106–8] These alcohols are manufactured in a similar way by the oxidation of a suitable fraction of petroleum in the presence of metaboric acid.[109]

Other uses claimed or described in the literature include the following, though few are extensively utilized in industry: neutron-absorbent shield for cooling and moderating nuclear reactors[110]; neutron scintillation counters[111,112]; electrolyte in a special electrolytic condenser[113]; plasticizers for natural and synthetic resins[114]; antioxidants in PVC and rubbers[115]; and purification of alcohols for perfume manufacture.[19] Glycol biborates have been suggested as insecticides and fungicides for the *in situ* treatment of timber.[116]

In the laboratory, borate esters find a number of uses: in Grignard syntheses for the preparation of alkylboron compounds[117]; analysis of boron-containing compounds—the boron is distilled as trimethoxyborane, hydrolysed and reacted with mannitol giving the mannitoboric acid complex, which also contains B–OR bonds[118]; preparation of other borate esters by transesterification[17]; and preparation of alkenes by pyrolysis of the metaborate.[60]

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SECTION A18

COORDINATION COMPOUNDS OF BORIC ACID

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Introduction

This section deals with compounds containing four-coordinate boron in a complex anion, whose formation has been established or inferred from the reaction of boric acid with organic compounds containing more than one hydroxyl group. Inorganic complexes with heteropolyacids are also described, although there is necessarily some overlap with Section A13, which treats compounds of this type in detail. An introductory survey of the equilibria leading to complex formation from boric acid in the presence of polyhydric alcohols is given and shows how an understanding of the subject was developed from studies of the effects of complex formation, their exploitation and comparisons of different complexants. Preparative and equilibrium studies are classified according to the reactants involved and the properties and applications of boric acid complexes are then reviewed.

General Survey

Recognition that boric acid may form anionic complexes with suitable organic compounds bearing two or more hydroxyl groups came initially from observation of the resulting acidity increase for boric acid.[1] This effect and the accompanying increase in electrical conductivity had first been recognized in the late nineteenth century, and historical aspects have received attention as part of a previous work.[2] Earlier relevant studies of the solubility of boric acid in the presence of organic complexants were reviewed in the first edition of the present volume.[3] The formation of anionic complexes from suitable polyhydric alcohols and boric acid was also manifest by the influence of the latter and other boron compounds on optical rotation[4,5,6] and by the behaviour of sugars during chromatography and electrophoresis[7,8] in the presence of borates. Conductivity changes on formation of borate complexes have also been recorded for a range of complexants.[9] Following its use in the titration of boric acid, the effect came to be exploited for the resolution and separation of sugars.[8,10,11] Later, as the stereochemical requirement for complex formation became appreciated[12,13,14], it was utilized for structural studies on complexants, e.g. α-hydroxy carboxylic acids[15,16,17], polyhydric alcohols[18,19,20] and sugars.[21,22,23,24] Generalized requirements for compounds to form complexes with boric acid developed from these observations, and they have been endorsed and extended by quantitative work providing equilibrium constants for the interactions involved. Since the first isolation of a salt containing the complex 'polyol–borate' anion[25] several such compounds have been isolated and studied. A cyclic ester structure was initially proposed for the boron-containing complex anion[26] but it was subsequently shown that the species had a spiran structure.[27,28,29,30] In particular the resolution of optical antipodes of the 1:2 boric acid: salicyclic acid complex supported this structure.[6,31]

The several effects of the formation of borate complexes, outlined above, were initially ascribed to solubility effects[32,33] and later to the formation of trigonal boron species.[26] However, the involvement of the tetrahydroxyborate anion in a complex-forming reaction with the polyhydric alcohol was initially supported by studies of the distribution of diethyl tartrate between ether and water containing various boron compounds.[34] The preference of this ester for the aqueous phase was found to be directly related to the ability of a dissolved boron compound therein to furnish the tetrahydroxyborate anion on ionization. The same relationship was observed for the effect of boron compounds on the optical rotation of diethyl tartrate[35], mannitol and fructose[36] and glucose.[37] The involvement solely of solubility effects has also been refuted by pH and freezing-point measurements on the boric acid-complexing sugar system.[38, 39] The interpretation of complex formation as arising from the reaction of a suitable polyhydric alcohol with the tetrahydroxyborate anion, giving an anionic complex of which the accompanying proton is acidic, was not disproven by the occurrence of non-acidic products[40] since it was later recognized that cyclic esters, or borolanes, containing trigonal boron could be formed.[41, 42] The involvement of the tetrahydroxyborate anion is supported by work showing that the presence of sodium hydroxide is necessary before mannitol will give an appreciable degree of complex formation with boric acid.[43] More recently, the formation of the tetrahydroxyborate anion from boric acid has been confirmed by both Raman spectroscopy[44] and ^{11}B N.M.R.[45], and its involvement in complex formation from boric acid and polyhydric alcohols has been supported by conductance[46], pH[47, 48] and ^{11}B N.M.R.[49] studies on this system.

The investigations outlined above show that complex formation in the system boric acid–polyhydric alcohol may be described by the following equilibria:

$$\mathrm{B(OH)_4^- + PH_2 \rightleftharpoons BP(OH)_2^- + 2H_2O} \quad . \ . \ . \ . \ . \ (1)$$

$$\mathrm{B(OH)_4^- + 2PH_2 \rightleftharpoons BP_2^- + 4H_2O} \quad . \ . \ . \ . \ . \ . \ (2)$$

$$\mathrm{B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+} \quad . \ . \ . \ . \ . \ . \ (3)$$

where PH_2 represents the polyhydric alcohol capable of acting as a bidentate ligand and forming, with the tetrahydroxyborate anion, a complex anion having the spiran structure depicted in Fig. 1 for an aliphatic 1,2-diol.

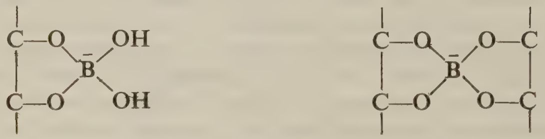

Fig. 1

Independent reports in closest agreement[50,51] give values of $5{\cdot}79 \times 10^{-10}$ and $5{\cdot}98 \times 10^{-10}$ for the ionization constant of boric acid, K_a (equation 3 above), in aqueous solution at 25°C. The concentration of the resulting tetrahydroxyborate anion is enhanced at high pH, whilst the formation of neutral esters from boric acid and polyhydric alcohols (equation 4) is promoted at low pH.

$$\mathrm{B(OH)_3 + PH_2 \rightleftharpoons PB(OH) + 2H_2O} \quad . \ . \ . \ . \ . \ . \ (4)$$

In the tables that follow, equilibrium constants for the formation of complex borate anions are designated k_1 and k_2; they refer respectively to the formation of the anions $BP(OH)_2^-$ and BP_2^- from the tetrahydroxyborate anion (equations 1 and 2). For the same equilibria written as involving boric acid it follows that the respective equilibrium constants (k'_1 and k'_2) are:

$$k'_1 = k_a k_1 \quad \text{and} \quad k'_2 = k_a k_2.$$

If the two complex anions are viewed as interconvertible, then it also follows that the equilibrium constant for the production of the anion BP_2^- is given by k_2/k_1.

It has been observed that there is an appreciable variation in the magnitude and ratio of equilibrium constants for the formation of borate complexes by various hydroxylic organic compounds. The outline above shows how consideration of these differences contributed to an understanding of the reaction. For simple aliphatic diols complex formation is effectively confined to those bearing vicinal hydroxyl groups either adjacent or separated by one chain position. A *cis* rather than *trans* conformation of these hydroxyl groups is best suited to complex formation from boric acid in the case of aliphatic diols. Since free rotation about the carbon chain allows adjacent hydroxyl groups to assume a *trans* orientation, and is encouraged by their mutual repulsion, so simple aliphatic diols have relatively low equilibrium constants for complex formation.[9] As the number of hydroxyl groups increases above two this effect may make only successively smaller reductions in the net number of hydroxyl groups orientated to favour complex formation, so that the linear sugar alcohols are among those compounds with the greatest tendency to form complex anions with boric acid. These generalizations also follow by comparing the oxygen–oxygen separation in the tetrahydroxyborate anion, 2·40–2·44 Å[52], with the separation and conformation of hydroxyl groups in the diol or polyhydric alcohol.[7] There is some preference for 1,2-diols to form complex anions whilst esterification (equation 4) may be the dominant interaction with 1,3-diols.[53, 54, 55] This observation has been rationalized by matching the tetrahedral and trigonal planar boron structures, present respectively in the complex and ester, with the ring structures resulting from the two different diols in these products.[55] The tetrahedral tetrahydroxyborate anion for example is best accommodated in the five-membered ring formed from its interaction with a 1,2-diol. Complex formation by saturated alicyclic polyhydric alcohols is possible, although examples are confined mainly to five- and six-membered ring compounds having adjacent hydroxyl groups. Puckering of a saturated six-carbon ring may make the *trans* orientation of adjacent hydroxyl groups best suited to complex formation, whilst allowing complex formation by a *cis* conformation of hydroxyl groups in the 1,3,5-positions.[56] Saturated five-carbon ring compounds have been found to require a *cis* conformation of hydroxyl substituents to allow complex formation. With hydroxyl groups on a cyclic substrate the effect on their conformation when the substrate departs from planarity is especially significant for ring sugars, polysaccharides and related natural products. In such cases the conformation of the hydroxyl groups is often more usefully expressed by the angle between the planes in which they lie relative to the carbon–carbon axis since this, unlike the customary *cis* and *trans* labels, includes the effect of ring distortions. Comparison of different results in such compounds is also complicated further by mutarotation.

Among aromatic compounds complex formation by diphenols has been found to require adjacent hydroxyl groups in an *ortho* relationship, whilst in condensed aromatic systems complex formation is also possible for hydroxyl groups spanning the bridging site, e.g. in 1,8-naphthalene diol. It seems likely that in some cases reaction between the phenolate anion and boric acid contributes to complex formation involving phenolic hydroxyl groups. Studies of complex formation by nuclear substituted benzene derivatives have shown that an electronegative substituent favours complex formation, and this could well be because reaction with the tetrahydroxyborate anion and stabilization of the resulting complex anion may both be enhanced thereby. A single phenolic hydroxyl group may also participate with adjacent primary alcohol or carboxylic acid groups in the formation of a complex borate anion, and rotation about the carbon–oxygen bond may encourage a suitable disposition of the hydroxyl groups. Complex formation is also particularly marked with aliphatic α-hydroxycarboxylic acids whilst β-hydroxycarboxylic acids are apparently without action.[9] Hydration of the carbonyl group has been proposed as a contribution to this effect[9] and enol formation may also be involved, since only with a β-hydroxycarboxylic acid enol would bond rotation be able to produce the *trans* conformation of hydroxyl groups which disfavours complex formation. It is also generally accepted that enol formation is responsible for complex formation at low pH between boric acid and suitable carbonyl compounds, which may result in highly coloured products.

Complex formation by boric acid with polyhydric alcohols and related compounds has been the subject of several general reviews[7, 9, 57] which have also included a survey of the history of the effect and presented rationalizations involving structural considerations.[7,9,12] Reviews have also emphasized the use of complex formation for structural studies on the complexants[8,9,12,58] and have dealt with the structure of the complexes themselves.[59] The formation of borate complexes from polysaccharides[60] and from complexing groups as components or chemical constituents of biological materials has also been reviewed[59,61], and an extensive survey of boric acid complexes and their isolation has been published.[2]

Although as reactants the heteropolyacids and related inorganic compounds merit a separate treatment, the process of complex formation is formally analogous to that with organic complexants, since suitably orientated hydroxyl groups in the acid structure lead to the formation of a complex borate anion. The structure of the acids has been reviewed[62] and their reaction products with borates are treated later in this section.

Reactants

Aliphatic and Alicyclic Dihydric Alcohols

The interaction of boric acid with dihydric alcohols leading to a complex anion containing four-coordinate boron may be complicated, since reactions resulting in borate esters (Section A17) can accompany or supplant complex formation[63,64], and there may also be formed borolane esters (equation 4) which can themselves give salts under suitable conditions. Examples of complex formation from boric acid and vicinal aliphatic and alicyclic diols have been restricted to 1,2- and 1,3-diols, despite a report of complex formation in an aromatic 1,4-diol system.[65] In most cases complex formation from these simple alcohols is relatively weak.

As a result of comparative studies of the esterification and complexation of boric acid by several aliphatic 1,2- and 1,3-diols[54] it has been noted that 1,3-diols favour the formation of neutral esters whilst 1,2-diols prefer to form complexes. This observation was rationalized[55] by matching the stereochemistry of tetrahedral and trigonal boron with the ring structures resulting from the formation of complexes and esters. Trigonal boron present in the ester, for example, is best accommodated by the six-membered ring resulting from a 1,3-diol.

Complex formation from boric acid and vicinal diols was evidenced at an early stage by electrical conductivity measurements made upon boric acid in the presence of glycols[9,66], and it was also recognized from structural studies that neutral esters could be formed.[40,42] More recently complex formation from boric acid and several diols has been studied by an ion-exchange method leading to the determination of equilibrium constants for complex formation from ethylene glycol, propylene glycol, butylene glycol and glycerol.[67] Electrical conductivity measurements have also shown that methyl-substituted derivatives of glycerose, the oxidation product of glycerol, may form a complex with boric acid.[68] Raman spectroscopy has been used to examine the formation of 1:1 and 1:2 boric acid:diol complexes from several 1,2- and 1,3-diols[69] and pH measurements have been used to determine equilibrium constants for the formation of borate complexes by several compounds including 1,2- and 1,3-diols[48] (Table I). Ionization constants of the boric acid–ethylene glycol complex have also been obtained from spectrophotometric studies.[70] In other work some 1,2- and 1,3-diols were separated by crystallization of their borate complexes.[53]

Generally, the simple diols show only low equilibrium constants for complex formation with boric acid. For ethylene glycol and boric acid studies both of the deviations of physical properties from simple additivity[71] and examination of the products after evaporation[72,64] have shown that neutral esters may also be produced. The formation of complexes from boric acid and isomeric 2,3-butanediols has been examined[73]; and in a study of complex formation by several other diols Raman spectroscopy has been used to show that 1,2-ethanediol forms both 1:1 and 1:2 borate:diol complexes.[69] A 1:1 borate:diol complex has been prepared from pinacol[74] and the formation of a neutral ester has also been established.[75] Crystals of alkali-metal dipinacol borates have also been formed from the components in aqueous solution.[76] The formation of salts of 1:1 borate complexes with cyclohexane- and cyclopentane-diol has been examined[31] and the conformation of some five- and seven-carbon alicyclic diols has been studied through the formation of borate complexes.[19] Paper ionophoresis has been used to examine the formation of boric acid complexes from several cyclitols having a *cis* 1,2-diol grouping.[77] More recently the formation of a borate complex by *cis*-3,4-dihydroxytetrahydrofuran has been studied by proton N.M.R.[78]

Table I.—Equilibrium Constants for the Formation of Boric Acid Complexes from 1,2- and 1,3-Diols

Compound	k_1	k_2	Reference
Ethylene glycol	1·85	0·1	
Propylene glycol	3·10	1·60	
2,3-Butanediol	3·45	4·85	
Phenyl-1,2-ethanediol	7·45	7·16	
3-Methoxy-1,2-propanediol	18·8	13·4	
Glycerol	16·0	41·2	
Catechol	$7·80 \times 10^{3}$	$1·42 \times 10^{4}$	
Polyvinyl alcohol	1·80	4·30	
Pentaerythritol	$2·4 \times 10^{2}$	$1·11 \times 10^{3}$	(48)
1,2-Ethanediol	2·15	1·15	
1,2-Propanediol	4·05	3·85	
1,3-Propanediol	1·27	0·11	
1,2,3-Propanediol	14·0	57·9	
L-2,3-Butanediol	37	$1·64 \times 10^{2}$	
Meso-2,3-butanediol	2·7	4·6	
2-Methyl-2,3-butanediol	18	$2·1 \times 10^{2}$	
2,3-Dimethyl-2,3-butanediol	11	$2·16 \times 10^{2}$	
cis 1,2-Cyclopentanediol	26	$1·42 \times 10^{2}$	
cis 1,2-Cyclohexanediol	1·0	0·7	(79)
Ethylene glycol	—	0·10	
Propylene glycol	—	1·60	
Butylene glycol	—	4·85	
3-Methoxy-1,2-propanediol	—	13·40	(80)

Aliphatic and Alicyclic Polyhydric Alcohols

General aspects of the reaction of borates with polyhydroxy compounds have been reviewed elsewhere.[57] The formation of a glycerol–boric acid complex has been studied by pH measurements[81,82] and the system has also been the subject of earlier investigations.[83] The alkali titration of boric acid in the presence of glycerol has been examined[84] and used to estimate a dissociation constant for the boric acid–glycerol complex.[85] Titration studies have also shown the dependence of the acid properties of boric acid–glycerol mixtures upon the concentration of the latter[86], and the influence of temperature and glycerol concentration on complex formation in this system has been examined.[87] The phase diagram for the system boric acid–water–glycerol has been determined[88] and refractive index and specific gravity measurements have been made on mixtures of these components.[89] Differential potentiometric measurements have shown that at 25°C in boric acid and glycerol solutions containing potassium chloride (0·1M) the p*K* values for formation of complex acids of the type HBP and HBP_2 are respectively 7·45 and 7·19.[90] In other work the absorption of glycerol by ion-exchange resins has been found to be increased by their treatment with boric acid.[91,92] Lanthanide salts of a boric acid–glycerol complex have also been formed and were precipitated from alkali solution by adding ammonia and acetone.[93]

It has been shown that concentrated equimolar solutions of boric acid and pentaerythritol may form a polymeric complex[54] and similar products have been formed by heating the solid components.[94,95] Chelation constants for the formation of 1:1 and 1:2 borate:pentaerythritol complexes have been determined from potentiometric measurements.[96] Preparative studies have also been performed for salts formed by borate–pentaerythritol complexes with alkali metals[97,98], ammonia[98], calcium[99], strontium and barium[100] and zinc and cadmium.[101] Nickel[102] and both cobalt and manganese[103] ammonia-containing salts of this complex anion have also been prepared. In these studies thermogravimetric data have been recorded for the products and their structures have also been examined by infra-red spectroscopy[97, 98, 101, 102] and *X*-ray methods.[95, 98, 103]

A dialysis method has been applied to show that the reaction of boric acid and polyvinyl alcohol leads to a 1:1 complex, and thermodynamic constants for its formation were obtained.[104] The effect of boric acid upon the viscosity of polyvinyl alcohol has also been examined[105] and *X*-ray studies have been performed on the reaction of boric acid with solutions of polyvinyl alcohol[106, 107] and with polyvinyl alcohol fibres.[107] Polyvinyl alcohol and boric acid have been shown to give a characteristic blue colouration in the presence of iodine.[108, 109] Absorption bands for this system have been studied[110, 111] and there is evidence that a borate–iodine complex is involved.[111]

Complexes formed by boric acid with 2-methyl-2-(hydroxymethyl)-1,3-propanediol have been studied[112, 113] and sodium and barium salts of the complex of boric acid with 2,2-bis-(hydroxymethyl)-3-methyl-1-butanol have been prepared.[114] In other work Group IA metal[115, 116, 117] and Group IIA metal[116, 118] salts of a complex of boric acid with 2-ethyl-2-methylol-1,3-propanediol have also been prepared and examined. The formation of boric acid complexes by some cyclitols having *cis*-1,3,5-hydroxy groups has been studied[56] and equilibrium constants for the formation of boric acid complexes with several quercitol and inositol isomers were measured. For *cis*-inositol the equilibrium constant for the formation of a 1:1 borate complex was found to be $1{\cdot}1 \times 10^6$.[56] Complex formation between boric acid and scyllitol has also been studied.[119, 120]

Sugars and Sugar Alcohols

The literature contains many reports of both quantitative and qualitative studies of the formation of complexes by borates with sugars and sugar alcohols. Where equilibrium constants have been determined for complex formation they show some variation for different experiments and this is particularly in evidence for mannitol, the single compound which has received most attention. To a large extent these differences are due to variations in ionic background, mutarotation and isomerization of the sugars studied. They also reflect the simplifying approximations necessary for the calculation of complexation equilibrium constants from experimental data.

Equilibrium constants for the formation of borate complexes by a range of sugars have been obtained from pH measurements[80, 121, 122, 123, 124] and values have also been calculated from paper ionophoresis experiments[125] (Table II). The influence of some sugars on the dissociation of boric acid has been studied[126, 127] and pH and conductance measurements have been made upon boric acid in the presence of several sugar alcohols and their anhydrides.[128] Studies have also been made of the effect of boric acid upon the optical rotation of complexing sugars.[129] In other work the pH, ultra-violet absorption and titration curve of boric acid in the presence of sugars has been studied.[130] The neutralization curves of boric acid in the presence of mannitol and fructose have been examined[38, 85] and pH measurements have been made upon boric acid containing hexose sugars.[131, 132] Results have been presented for the potentiometric titration of boric acid in the presence of several sugars.[133, 134] The chelation of boric acid by some pentose[135] sugars has been studied and polarographic reduction has been used to examine the formation of a fructose–boric acid complex.[136] Equilibrium constants have also been obtained for the formation of boric acid complexes from hexose sugars, and the corresponding thermodynamic functions ΔG°, ΔH° and ΔS° have been calculated.[137] In other quantitative studies of a range of hexose sugars it was found that the 1:2 borate:sugar complex predominated[80, 123], and complexes from hexoses and ketohexoses were found to be more stable than those from the aldohexose and aldopentose sugars examined.[80] These results were related to the sugar structure and the possibility of lactol formation.[80] More recently ^{11}B N.M.R. spectroscopy has been used to determine the ring size of complexes formed from boric acid and several sugars.[138]

A phase diagram has been obtained for the system boric acid–sorbitol–water[139] and pH measurements have been used to calculate equilibrium constants for the formation of boric acid complexes by sorbitol and mannitol.[140] Alkali-metal and alkaline-earth

Table II.—Equilibrium Constants for the Formation of Boric Acid Complexes from Sugars

Sugar	k'_1	k'_2	k_1	k_2	Reference
Arabinose	—	—	—	$1{\cdot}45 \times 10^{4}$	
Fructose	—	—	—	$2{\cdot}75 \times 10^{6}$	
Galactose	—	—	—	$1{\cdot}41 \times 10^{3}$	
Mannitol	—	—	—	$2{\cdot}75 \times 10^{6}$	
Xylose	—	—	—	$1{\cdot}58 \times 10^{4}$	(121)
Mannitol	—	—	$5{\cdot}60 \times 10^{2}$	$1{\cdot}16 \times 10^{5}$	
Fructose	—	—	$6{\cdot}90 \times 10^{2}$	$0{\cdot}83 \times 10^{5}$	(122)
d-Galactose	$1{\cdot}64 \times 10^{-7}$	$1{\cdot}94 \times 10^{-7}$			
d-Glucose	$1{\cdot}87 \times 10^{-7}$	$5{\cdot}74 \times 10^{-7}$			
d-Mannose	—	$2{\cdot}63 \times 10^{-5}$			
d-Fructose	$3{\cdot}75 \times 10^{-6}$	$8{\cdot}67 \times 10^{-5}$			(123)
D-Ribose			—	$1{\cdot}570 \times 10^{7}$	
D-Arabinose			—	$1{\cdot}892 \times 10^{3}$	
L-Arabinose			—	$3{\cdot}565 \times 10^{3}$	
D-Xylose			—	$1{\cdot}016 \times 10^{4}$	
D-Lyxose			$6{\cdot}607 \times 10^{4}$	—	(135)
d-Fructose	$3{\cdot}84 \times 10^{-4}$	$1{\cdot}02 \times 10^{-5}$			
d-(+)-Glucose	$9{\cdot}50 \times 10^{-3}$	$2{\cdot}33 \times 10^{-3}$			
d-(−)-Mannitol	$1{\cdot}00 \times 10^{-4}$	$1{\cdot}29 \times 10^{-5}$			(124)
D-Fructose			$3{\cdot}0 \times 10^{3}$	$1{\cdot}24 \times 10^{5}$	
D-Galactose			$1{\cdot}75 \times 10^{2}$	$4{\cdot}28 \times 10^{2}$	
D-Glucose			$1{\cdot}50 \times 10^{2}$	$7{\cdot}60 \times 10^{2}$	
D-Mannose			$1{\cdot}02 \times 10^{2}$	$4{\cdot}58 \times 10^{2}$	(137)
D-Mannose			50	$4{\cdot}9 \times 10^{2}$	
D-Glucose			80	$7{\cdot}7 \times 10^{2}$	
L-(+)Arabinose			$1{\cdot}3 \times 10^{2}$	$6{\cdot}75 \times 10^{2}$	
D-(+)-Galactose			$1{\cdot}27 \times 10^{2}$	$2{\cdot}98 \times 10^{2}$	
Fructose			—	$9{\cdot}50 \times 10^{4}$	(48)
α-D-Glucose			$1{\cdot}35 \times 10^{2}$	$8{\cdot}70 \times 10^{2}$	
D-Mannitol			$1{\cdot}10 \times 10^{2}$	$1{\cdot}37 \times 10^{5}$	(79)
L-Rhamnose			—	$4{\cdot}093 \times 10^{2}$	
D-Galactose			—	$2{\cdot}427 \times 10^{2}$	
D-Glucose			—	$7{\cdot}178 \times 10^{2}$	
D-Arabinose			—	$1{\cdot}892 \times 10^{3}$	
L-Arabinose			—	$3{\cdot}565 \times 10^{3}$	
D-Xylose			—	$1{\cdot}016 \times 10^{4}$	
D-Mannose			—	$3{\cdot}289 \times 10^{4}$	
D-Fructose			—	$1{\cdot}084 \times 10^{5}$	
L-Sorbose			—	$6{\cdot}266 \times 10^{5}$	
D-Mannitol			—	$8{\cdot}241 \times 10^{4}$	
D-Dulcitol			—	$1{\cdot}690 \times 10^{5}$	
D-Sorbitol			—	$4{\cdot}436 \times 10^{5}$	(80)

metal salts of borate xylitol complexes have been prepared[141, 142, 143, 144] and have been characterized by infra-red and thermogravimetric measurements. Similar studies have been made of the formation of boric acid complexes with dulcitol.[145] The thermal reaction product of solid boric acid with xylitol has been studied[146] and conductivity measurements have been reported for complexes of boric acid with xylitol, arabitol and adonitol.[147] The effect of sugar alcohols and their anhydrides on the dissociation of boric acid has been studied[148, 149] and the anhydrides were found to be less effective that the corresponding alcohol.[148] Titration curves have been recorded for boric acid in the presence of mannitol[150], sorbitol and sorbitan[151] and mannitan[38] in investigations of complex formation, and pH measurements have been made for boric acid on the formation of a complex with erythritan.[152] A study of the evaporation of ammonia in the presence of boric acid and complexing sugars has demonstrated that they compete with ammonia for reaction with boric acid[153], and the reaction of boric acid with sugars has been the subject of a general review.[58]

Mannitol was one of the earliest-studied complexants for boric acid[154] and initial studies used chemical techniques to examine the composition and hydrogen ion concentration in the system.[155] The stoichiometry of the boric acid–mannitol system has been examined more recently by using conductivity measurements[46] and the potentiometric method[46, 156], and equilibrium constants for complex formation were obtained from these studies. An examination of the borate–mannitol system using dilatometry has also been reported.[157] Reports that the borate–mannitol complex is not formed from boric acid in the absence of sodium hydroxide[43] and that lithium metaborate may be favoured over boric acid as a reactant[158] both confirm the involvement of the tetrahydroxyborate anion in complex formation. Other work on the boric acid–mannitol system has confirmed that even using a large molar excess of mannitol complex formation may not readily be detected with the boric acid concentration present in seawater.[159]

Quantitative studies of complex formation by boric acid with mannitol have been reviewed and literature values of appropriate equilibrium constants have been summarized.[160] The equilibrium constants reported by different workers are shown in Table III. The equilibrium constant for complex formation between boric acid and mannitol has been found to be proportional to the half power of the ionic strength of the solutions involved[161] and in other work[160] reported equilibrium constants[41] were corrected to infinite dilution and showed good agreement with the values obtained in a definitive study of the boric acid–mannitol–water system.[162] This latter study has also confirmed that both 1:1 and 1:2 borate:mannitol complexes may be formed, and other data[163] have been shown[164] to be consistent with this result. The composition of the borate–mannitol–water system has also been examined by an ion-exchange technique where the distribution of boric acid between an ion-exchange resin and aqueous mannitol was determined in relation to the concentration of the latter.[165] Raman spectroscopy of aqueous solutions of boric acid and mannitol has also shown that both 1:1 and 1:2 borate:mannitol complexes may form[166] and the composition of these mixtures has been the subject of investigations using potentiometry and polarimetry[167], cryoscopy[158], osmotic coefficient measurements[168], and the calorimetric determination of heats of neutralization of the complexes.[169] Equilibrium constants for the formation of boric acid–mannitol complexes have been determined from potentiometric measurements[170] by a calculation method which uses the apparent ionization constant of boric acid in the system when successive complexation equilibria are expressed in terms of a net equation.[161] This potentiometric method has also been used to determine the thermodynamic functions ΔH°, ΔG°, and ΔS° for the formation of complexes from boric

Table III.—Constants for the Formation of Boric Acid Complexes from Mannitol

k_1'	k_2'	k_1	k_2	Reference
—	—	—	$2{\cdot}75\times10^{6}$	(121)
—	—	$5{\cdot}60\times10^{2}$	$1{\cdot}16\times10^{5}$	(122)
$1{\cdot}00\times10^{-4}$	$1{\cdot}29\times10^{-5}$			(124)[a]
$2{\cdot}5\times10^{-6}$	$1{\cdot}1\times10^{-4}$			(41)
$1{\cdot}2\times10^{-6}$	$4{\cdot}4\times10^{-5}$			(160)[b]
$1{\cdot}62\times10^{-3}$	$1{\cdot}05\times10^{-5}$			(162)
—	—	$3{\cdot}0\times10^{2}$	$5{\cdot}1\times10^{4}$	(46)
$4{\cdot}39\times10^{-5}$	$6{\cdot}05\times10^{-6}$			(170)[c]
—	$1{\cdot}0\times10^{-4}$	—	—	(47)
—	—	1×10^{4}	$7{\cdot}727\times10^{4}$	(171)

[a] For *d*-(−)-mannitol.
[b] Values from Ref. 41 adjusted to zero ionic strength.
[c] At zero ionic strength.

acid and mannitol.[171] The equilibrium constant for the formation of a 1:2 boric acid: mannitol complex has also been obtained from pH measurements on solutions containing these two reactants[47], and the dissociation constant for a boric acid–mannitol complex has been obtained from other titration studies.[172] The 1:1 complex of boric acid with mannitol has been isolated from an aqueous mixture of the components[173] and a crystalline product was obtained from the reaction of mannitol and metaboric acid in acetone.[174] Complex products have also been isolated and studied from the dry heating of mannitol and boric acid.[175]

Measurements have shown an increase in the electrical conductivity of boric acid in the presence of α- and β-D-glucose, and several glucosides[176], indicating complex formation. Boric acid has also been found to decrease the optical rotation of glucose in aqueous solution[177] and other optical rotation and titration studies have indicated that the borate–glucose complex is stable only over a limited pH range.[178] Optical rotation measurements have also shown that the borate complex of phenyl-β-D-glucopyranoside exists only in alkaline solution.[179] A crystalline borate complex of D-glucose-5,6-carbonate has been prepared[78] and in the same work N.M.R. studies have indicated that the formation of a borate complex by 5-O-methyl-D-glucose proceeds with a pyranose into furanose conversion.[78] The formation of borate complexes by several osazone derivatives of D-glucose has also been studied.[180] It has been reported that borate hinders the reaction of glucose with acetone[181] and this may be due in part to the formation of a borate–glucose complex. It is also possible that complex formation makes a contribution to the observed stabilization of glucose during its thermal polymerization in the presence of metaboric and orthoboric acids.[182]

Oligosaccharides and Polysaccharides

The reaction of boric acid with polysaccharides has been reviewed[60, 183] and particular attention has been given to the higher molecular-weight polysaccharides with which complex formation leads to gelling.[60] Even at low excess concentrations, highly polymerized polysaccharides having adjacent *cis* hydroxyl groups, e.g. mannan, galactomannan and polymannuronic acid, have been observed to form gels with borax.[183] Gel formation is a consequence of cross-linking by complex formation and hydrogen bonding acting together and has been shown to be prevented by acid pH and to be reversed by the presence of low molecular-weight complexants competing for the borate.[183] Complex formation with boric acid has allowed studies of the structure of polysaccharides[184] and has been exploited for separating the component sugars of a polysaccharide by electrophoresis.[185] In other work the interaction of boric acid with amylose has been examined by gel filtration and an association constant calculated.[186]

In some early studies it was found that the disaccharide β-lactose gave an increase in the conductivity of boric acid solution, characteristic of complex formation, whilst α-lactose did not.[23] The absence of a conductivity increase with this latter compound, and with the disaccharides maltose and melibiose, was ascribed to the conformational lability of their pyranose forms.[23] Acidity measurements have given some evidence for complex formation by boric acid with sucrose[187] and the formation of borate complexes by the isomaltose series of polysaccharides has been examined in chromatographic studies[10, 11] which indicated that melibiose but not maltose forms a borate complex.[11] In other work the formation of borate complexes has been used to effect the chromatographic separation of several oligosaccharides on a column of a dihydroxyboryl ($>B(OH)_2$) substituted polymer.[188]

The tetrahydroxyborate anion has been reported to combine with cellulose[189] and it has also been reported that cellulose increases the acidity of boric acid in aqueous solution.[190] Studies of the formation of a borate complex by cellulose may however be complicated by the presence of sugars (e.g. mannose) therein.[191] Treatment of cellulose with saturated boric acid solution followed by heating gave cellulose containing a slightly higher boron loading than that for the appropriate 1:1 complex, and the product was reported to be stable under acid conditions.[192]

Glycosides

An outline of the interaction of aqueous borate with some nucleosides and nucleotides has been included in a review of borate–polyhydric alcohol compounds of biochemical interest.[59] Potentiometric measurements have shown that inosine and uridine, as well as D-ribose, form 1:2 complexes with boric acid, and formation constants were found to be $2{\cdot}63 \times 10^3$, $4{\cdot}79 \times 10^3$ and $1{\cdot}02 \times 10^3$, respectively.[193] Electrical conductivity and viscosity measurements have shown that a 2:1 glycoside:borate complex is also formed in the gelled mixture of boric acid, sodium hydroxide and guanosine.[194] In other work a monobasic acid complex has been prepared from boric acid and the cymarose glycoside *g*-strophthanthidin.[195] Other complex N-glycopyranoside salts have been prepared from the reaction of boric acid and an amine with D-mannose,[196] and with D-ribose[197], but a product of this type was not obtained from D-glucose.[196] A column of ion-exchange resin loaded with boric acid has been used to effect the separation of several ribose nucleosides.[198] More recently the formation of borate complexes has been examined and exploited for the chromatographic separation of several nucleotides.[199, 200]

Vitamins and Enzymes

A survey of the interaction of boric acid with vitamins has been included in a review of the reaction of boric acid with substances of biological interest.[61] In early studies it was found that boric acid acted to stabilize the activity of vitamins A, B and C toward heating and this may be a consequence of complex formation.[201] A complex formed from boric acid and vitamin B_6 has also been proposed as the species most likely to be formed from borate in plant tissues.[202] At low concentrations boric acid has been found to promote the synthesis of ascorbic acid during seed germination.[203] In other studies boric acid has been reported to increase the amount of dehydroascorbic acid produced from the oxidation of L-ascorbic acid and this may also be a consequence of complex formation acting to stabilize the product.[204]

Reports have appeared of the conditions and pH ranges appropriate to the formation of both 2:2, 2:1 and 4:2[205] and 1:2[206] borate:ascorbic acid complexes. The calcium and barium salts of these 2:1 and 1:1 complexes have been prepared from aqueous solution[207] and a cobalt tetra-amine salt of the 2:2 complex has been reported to be obtainable similarly as a plastic solid.[208] Alkali-metal salts of 2:4 borate:ascorbic acid complexes have also been prepared.[209, 210]

Riboflavin (Vitamin B_2) has been found to form a water-soluble compound on admixture with boric acid[211, 212] and borax has been found to exert a strong influence on the optical rotation of riboflavin in alkaline solution.[213] Thiamine (Vitamin B_1) in aqueous solution has also been found to be stabilized by the presence of borate.[214] Pyridoxine (Vitamin B_6), which contains a saligenin-diol grouping, has been found to form an addition compound with boric acid in the presence of hydrochloric acid.[215] The formation of a 2:1 borate:pyridoxine complex has also been established in other work[216, 217], and the structure of this complex has been examined by comparative thin-layer chromatography.[218]

Although the possibility of borate complex formation with any organic derivative bearing suitably orientated hydroxyl groups must be recognized, the literature contains no substantiated report of complex formation by boric acid with proteins as such. The effect of boric acid upon the activity of enzymes has been reviewed[61] and the topic is not treated in detail here. Although some inhibitory effects may be ascribed to the formation of a borate complex with either the enzyme or the polyhydroxy substrate involved, they may also arise from other interactions. Complexing functions present as constituents or components of enzymes may also fall into those classes which have been treated separately. There is a recent report that several enzymes may be made insoluble in water by complex formation with boric acid bound on a polymer support.[219]

Miscellaneous Natural Products

Boric acid has been found to give a fluorescent colour reaction with several flavonols in the presence of oxalic acid, and complex formation indicated by this effect has been proposed as responsible for the relatively high boron content of plants which contain flavonols.[220] A crystalline product was obtained from the reaction of boric acid and oxalic acid with the flavone quercetin in the presence of glacial acetic acid.[221] Other preparative and spectrophotometric studies have been made upon complexes formed in the presence of oxalic acid and boric acid from flavones, flavonols and chalcones.[222] A spiran structure with boric acid linked to the flavonoid oxygen via oxalic acid ligands was indicated for these species.[222] Boric acid has also been found to give a bathochromic shift in the spectrum of flavonoid compounds containing an *ortho* dihydroxyl grouping.[223]

A 1:1 complex has been found to be formed from boric acid with hydroxyl groups on the macrocyclic lactone ring of the antibiotic erythromycin[224], and this has been used in a purification procedure for erythromycin.[225] Several *cis*-α, β-dihydroxy steroids have also been purified by formation and decomposition of a borate compound[226, 227] which has been reported to contain two steroid molecules and one tetrahedral boron atom.[226]

Aromatic Compounds

The formation of borate complexes has been observed with aromatic compounds having two or more adjacent phenolic hydroxyl groups, and with compounds where a phenolic group is adjacent to a carboxyl group, a carbonyl group or a side-chain hydroxyl group. Of the diphenols, catechol and derivatives have been subjected to most study, and stereochemical aspects have received attention.[228] Equilibrium constants determined for the formation of boric acid complexes by catechol and some derivatives are summarized in Table IV. These values are generally high since in addition to the reaction scheme normally considered for polyhydric alcohols (equations 1, 2, 3), reaction of the catecholate anion with boric acid may also be responsible for complex formation. In some early work several salts of boric acid–catechol complex anions were isolated as precipitates from solutions of their components but it was found that the corresponding acids could not be isolated in the presence of water.[25] Catechol is apparently the only compound which gives a dialkoxy diol borate complex[25, 229] ($PB(OR)_2^-$), and its formation has been supported by ultra-violet absorption studies of pyridine salts of catechol–borate complexes.[230] Other work on the catechol–boric acid–water system has indicated that formation of a 1:1 complex is favoured over the formation of a 1:2 catechol:boric acid complex[231], and it has been confirmed that the stability of a catechol boric acid complex falls with increase in the proportion of catechol therein.[232] In other work alkali-metal and amine salts of borate–catechol complexes have been prepared by crystallization from aqueous solution[28, 29, 233, 234] and by heating the appropriate reactants.[235, 236] Salts of a borate complex with catechol bearing a nitro-substituent have also been prepared[234], and coloured complexes formed by boric acid with 4-phenylazo catechol derivatives in alcohol solution have been used in the detection of boron.[237, 238] Hydrolysis of tripyrocatechol diborate in the presence of a base has been reported to give the appropriate salt of a complex dipyrocatechol boric acid, whilst catalytic hydrogenation of this product gave *cis*-cyclohexanediol.[239]

Equilibrium constants for the formation of borate–catechol complexes have been obtained from potentiometric measurements.[240] It was reported that only 1:1 borate: catechol complexes were obtained and their formation was encouraged by substituents increasing the acidity of the diphenol.[240] Spectrophotometry has also been used with potentiometric measurements to establish a correlation between stability constants for borate–catechol complexes (BP^-) and the acidity constants of the corresponding substituted catechols.[241] Stability constants for the 1:1 boric acid:catechol complex of 3- and 4-nitropyrocatechol have been obtained by spectrophotometry[242], from polarographic studies[243] and from potentiometric measurements.[244] In the latter work only a 1:1 complex was found for a concentration of catechol less than or equal to 4×10^{-3}M. Other potentiometric measurements have shown that 1:1 and 1:2 boric acid:catechol complexes may be formed, and equilibrium constants for their formation were determined together with the thermodynamic functions ΔH°, ΔG° and ΔS°.[245]

Table IV.—Equilibrium Constants for the Formation of Boric Acid Complexes from Aromatic Compounds

	k_1'	k_2'	k_1	k_2	Reference
2,3-Dihydroxynaphthalene	$7{\cdot}94 \times 10^{-5}$	—	$1{\cdot}24 \times 10^{5}$	—	
2,3-Dihydroxynaphthalene-6-Sulphonic acid	$9{\cdot}02 \times 10^{-5}$	—	$1{\cdot}41 \times 10^{5}$	—	
Catechol	$6{\cdot}61 \times 10^{-6}$	—	$1{\cdot}03 \times 10^{4}$	—	
Catechol monosulphonic acid	$1{\cdot}84 \times 10^{-5}$	—	$2{\cdot}88 \times 10^{4}$	—	
Pyrogallol	$4{\cdot}42 \times 10^{-6}$[b]	—	$6{\cdot}91 \times 10^{3}$[c]	—	(240)[a]
3-Nitrocatechol	$3{\cdot}47 \times 10^{-4}$			—	
4-Nitrocatechol	$1{\cdot}74 \times 10^{-4}$			—	
3,5-Dinitrocatechol	$2{\cdot}24 \times 10^{-2}$			—	(242)
Protocatechualdehyde	$1{\cdot}118 \times 10^{-4}$				(250)
Salicylic acid (anion)	$21{\cdot}7$	—	—	—	(279)
L-Noradrenaline	$1{\cdot}802 \times 10^{-5}$				
DL-Noradrenaline	$1{\cdot}298 \times 10^{-5}$				(298)
3,4-Dihydroxybenzoic acid (dianion)	$9{\cdot}70 \times 10^{-6}$	—			(299)
Pyrogallol	$8{\cdot}846 \times 10^{-6}$	4×10^{-5}			(257)
3,4,5-Trihydroxybenzoic acid (anion)	$1{\cdot}366 \times 10^{-5}$	—			(258)
2,3-Naphthalenediol	$9{\cdot}722 \times 10^{-5}$	—			(265)
2,3-Naphthalenediol	$5{\cdot}715 \times 10^{-5}$	—			(267)
-6-Sulphonic acid (anion)	$1{\cdot}731 \times 10^{-4}$[d]	—			(266)
3-Nitrocatechol	$2{\cdot}88 \times 10^{-4}$	—			
4-Nitrocatechol	$1{\cdot}02 \times 10^{-4}$	—			(243)
Catechol	—	—	$9{\cdot}376 \times 10^{3}$	$1{\cdot}832 \times 10^{4}$	(245)
Catechol	$7{\cdot}41 \times 10^{-6}$	—	$1{\cdot}16 \times 10^{4}$	—	
4-Chlorocatechol	$1{\cdot}35 \times 10^{-5}$	—	$2{\cdot}11 \times 10^{4}$	—	
4-Chloroacetylcatechol	$4{\cdot}47 \times 10^{-5}$	—	$6{\cdot}98 \times 10^{4}$	—	
4-Nitrocatechol	$1{\cdot}23 \times 10^{-4}$	—	$1{\cdot}92 \times 10^{5}$	—	
Tetrachlorocatechol	$7{\cdot}94 \times 10^{-4}$	—	$1{\cdot}24 \times 10^{6}$[c]	—	(241)

[a] For solutions having a molar excess of boric acid to complexing organic.
[b] Mean of two cited values.
[c] Calculated for comparison using k_a for boric acid $= 6{\cdot}40 \times 10^{-10}$.
[d] Corrected to zero ionic strength.

Sulphonation of catechol has been found to increase its equilibrium constant for formation of a borate complex in the case of catechol-4-sulphonic acid[240] and catechol-3,5-disulphonic acid[246], and this may be due to the sulphonate group increasing the acidity of the diphenol and acting to stabilize the complex borate anion. A potentiometric study of the formation of a borate complex by adrenaline has shown that a 1:1 complex predominates[247], and the formation of a borate complex by the catecholamine noradrenaline has been studied quantitatively by the potentiometric method.[248] Equilibrium constants have also been obtained for the formation of boric acid complexes by 3,4-dihydroxybenzoic acid[249] and the corresponding aldehyde derivative of catechol, protocatechualdehyde.[250] Complex formation by boric acid with these compounds and similar derivatives of pyrogallol has also been studied by ultra-violet spectroscopy and ion-exchange effects.[251]

Electrical conductivity measurements[252–254] and pH determinations[255] have indicated that boric acid may form highly ionized complex acids with polyphenols, e.g. pyrogallol and catechol tanning extracts, and titration studies have shown that 3,4,5-trihydroxybenzoic acid (gallic acid) may form a borate complex.[256] The potentiometric method has been used to determine equilibrium constants for the formation of boric acid complexes by pyrogallol[257] and gallic acid[258] and in both studies 1:1 complexes were found to be preferred. Boric acid has also been reported to form complexes with the phenolic compounds occurring in natural vegetable tanning materials[259] and particularly with tannins containing gallic acid, ellagic acid and glucosides[260] and quebracho or valonia tannins.[261] Boric acid has also been found to form a complex with hydroxyhydroquinone, and an equilibrium constant and a rate constant for the dissociation of this product have been reported from chronopotentiometric studies.[262]

The solubility curve of the system *cis*-tetrahydronaphthalene-1,2-diol–boric acid–water at 25°C has been determined[263] and both tetrahydronaphthalene-1,2- and -1,3-diol have been found to increase the electrical conductivity of boric acid solutions.[264] Complex formation by boric acid with 2,3-naphthalene diol[265] and 2,3-dihydroxy-6-naphthalenesulphonic acid[266] has been studied quantitatively. It was found that formation of a 1:1 boric acid:diol complex was preferred, particularly in the case of the sulphonated diol, and that the equilibrium constant for complex formation was also increased through the sulphonation. Other work on these complexants is in agreement with the equilibrium constant for complex formation from 2,3-naphthalene diol[240] but indicates a smaller equilibrium constant for formation of a borate complex from the corresponding sulphonate anion.[240, 267] Boric acid has been found to form both 1:1 and 1:2 borate:diol complexes with 4,5-dihydroxy-2,7-naphthalenedisulphonic acid (chromotropic acid) in dilute solution at acid pH[268], and stability constants have been determined for the formation of 1:1 and 1:2 borate:diol complexes from 2-bromo- and 2,7-dibromochromotropic acid.[269] At acid pH boric acid has also been found to form a coloured complex with the disodium salt of 3-(*p*-nitrophenylazo)-chromotropic acid.[270]

Spectrophotometric studies have shown that boric acid may form coloured complexes with dihydroxy anthraquinones and complex formation by boric acid with 1,2-dihydroxyanthraquinone (alizarin)[271] and its sulphonated derivatives[272, 273] has been examined. An optimum pH of 8 was reported for complex formation.[271] The reaction between the complex formed by sulphonated alizarin (alizarin S) and lanthanide ions has been ascribed to replacement of boron therein[272, 274], although formation of a lanthanide salt of the complex anion is a further possibility. In the presence of sulphuric acid boric acid has also been found to form coloured complexes with alizarin[275] and 1,5-diamino-4,8-dihydroxyanthraquinone[276] and the colour reaction of boric acid with some naphthaquinones and anthraquinones in the presence of citric acid has been examined.[277]

Aqueous solutions of boric acid have been shown to undergo a large increase in electrical conductivity in the presence of salicyclic acid[278], and a dissociation constant of $4{\cdot}6 \times 10^{-2}$ has been reported for the 1:1 complex of boric acid with salicylic acid.[279] From other studies of the formation of 1:1 and 1:2 borate:salicylic acid complexes it was concluded that in addition to the salicylate anion the free acid must be present for formation of the 1:2 complex.[280] The ultra-violet absorption spectrum of *p*-aminosalicylic acid in the presence of borax also shows bathochromic shifts that may be ascribed to the formation of borate complexes.[281] The formation of 1:1 and 1:2 boric acid:salicyclic acid complexes has been studied potentiometrically and the 1:1 complex was found to predominate at pH 2–4.[282] Stability constants for the formation of boric acid–salicylic acid complexes have been determined by infra-red spectroscopy[283] and the reduction of these complexes has been examined by polarography.[284] Thermal conductivity measurements have been used to study the formation of a 1:1 boric acid: *p*-aminosalicylic acid complex.[285] Quaternary ammonium salts of boric acid complexes with salicylic acid and hydroxynaphthoic acid have been obtained as crystalline products[286] and several metal salts of salicylic acid–boric acid complex anions have been prepared.[287] Salts formed by this same anion with tetra- and hexa-ammine complexes of cobalt, nickel and chromium have also been isolated.[288] The formation of a mixed copper borate–salicylate anion has also been studied.[289]

Electrical conductivity measurements have indicated that 2-hydroxybenzyl alcohol

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(saligenin) may form a complex with boric acid[290] and alkali-metal salts of this complex anion have been prepared from the synthesis of saligenin derivatives in the presence of boric acid or sodium metaborate.[291–293] More recently the formation of a boric acid–saligenin complex has been studied by ^{11}B N.M.R. spectroscopy.[65]

Carbonyl Compounds; Aldehydes, Ketones, Keto- and Dicarboxylic Acids

The diketone glyoxal has been found to form a complex with the tetrahydroxyborate anion, and a value of $2{\cdot}8 \times 10^5$ for the association constant of glyoxal with this borate anion was reported.[294] Polarographic studies have also shown that a 1,2-diphenylethanedione (benzil or diphenyl glyoxal) gives a 1:2 complex with boric acid and both equilibrium and rate constants were reported for the reaction leading to its formation.[295] Boric acid has been shown to react with curcumin in the presence of a mineral acid to give a coloured 1:2 boric acid:curcumin complex (rosocyanin) which was isolated.[296] In the presence of oxalic acid curcumin forms a further complex with boric acid[297, 298] which contains equimolar proportions of boric acid, curcumin and oxalic acid.[297] The structure of this product (rubrocurcumin) has been assigned[297] by comparison with the structure of rosocyanin[296] and subsequent work has confirmed these structures for rosocyanin[299] and rubrocurcumin.[299, 300] Infra-red spectra have been recorded for both complex products[301] and dissociation constants of boric acid–curcumin chelates have been measured.[302] The formation of a coloured curcumin complex has been used for the determination of micro amounts of boron and interference with this colour reaction has been observed from the presence of other complexing agents, e.g. mannitol.[303] Mixed borate complexes formed from diketones and carboxylic acids or their anhydrides have also been reported.[304] In other studies visible spectroscopy has indicated that at low concentrations and in the pH range 4·5–8·0 the aromatic ketone 9-(*p*-nitrophenyl)-fluorone forms a 1:1 complex with boric acid.[305]

Several *o*-hydroxycarbonyl compounds have been found to give a melting-point depression on admixture with boric acid and this has been ascribed to compound formation.[306] In other work colour reactions observed with boric acid in the presence of sulphuric acid and hydroxy- and amino-anthraquinones[307] and a range of other hydroxycarbonyl compounds[277] were ascribed to the formation of borate esters.[308] Despite the possible conversion of a hydroxycarbonyl compound to the enol form at acid pH it has not been conclusively shown that formation of a borate complex by this derivative is responsible for the colour reactions described.

Electrical conductivity measurements have indicated that α-keto carboxylic acids may form complexes with boric acid. Pyruvic acid has been found to produce a large increase in the conductivity of boric acid[309] and the effect has been attributed to complex formation after hydration of the carbonyl group. Further studies of the keto acids having no hydrogen atoms in the α-position to the carbonyl group and with which enol formation is therefore impossible have supported this interpretation. In particular conductivity increments were observed for boric acid with trimethyl pyruvic acid[310–312] and phenyl glyoxylic acid.[12, 313] Conductivity increments with these compounds were however less than those for equivalent concentrations of pyruvic acid. It has also been observed that β-keto acids form 1:1 complexes with boric acid and the products exhibited strong ultra-violet absorption.[314] Boric acid has also been shown to form a complex with some γ-pyronecarboxylic acids.[315] Complex formation by boric acid with chelidonic, meconic and comenic acids has been attributed both to enol formation and to hydration of the carbonyl group.[315] A dissociation constant of 4×10^{-2} has been reported for the complex of boric acid with meconic acid.[279] Neutralization curves obtained for mixtures of boric and oxalic acids have also indicated that complex formation occurs[316, 317] and this has been supported by a study of the solubility of boric acid in aqueous solutions of oxalic acid.[318]

Hydroxycarboxylic Acids

Complex formation has been observed for boric acid with hydroxy-acids ranging from the simple mono-hydroxy monobasic acids, e.g. lactic acid, to the mono- and poly- basic polyhydroxy-acids. In the latter class of compounds particular attention has been given to tartaric acid, trihydroxyglutaric acid and acids derived from the partial oxidation of complexing sugars. The carboxylic hydroxyl group necessarily participates in complex formation by a monohydroxy-acid whilst with a polyhydroxy-acid participation of this hydroxyl group in complex formation is generally encouraged by low pH. Early studies examined the increase in the electrical conductivity of boric acid as a consequence of complex formation from a range of hydroxy monocarboxylic acids.[319, 15, 320, 9] In contrast to the α-hydroxy carboxylic acids it was found that several β-hydroxy carboxylic acids were without effect upon the conductivity of boric acid.[319, 9] It was initially suggested that the effect of α-hydroxy carboxylic acids was due to hydration of the carboxylic carbonyl group[319, 9] and the ineffectiveness of the β-hydroxy acids was ascribed to repulsion between hydroxyl groups in the β-position and on the hydrated carbonyl group.[9] Comparison of the structures of these acids also shows that the six-membered ring present in a borate complex formed from the β-hydroxy acid is non planar, and this may be the dominant influence inhibiting complex formation. It is also possible that the enol form of the acid contributes to complex formation, since only with a β-hydroxy-acid could bond rotation result in a conformation that disfavours this interaction. Attention has been given to steric effects in the formation of borate complexes from cyclic hydroxy-acids.[16]

From electrodialysis studies[321] and potentiometric titration[322] it has been shown that boric acid may form complex anions of the type BP^- and BP_2^- with lactic acid. Electrical conductivity and ion exchange studies have also been reported to indicate the formation of a 2:3 boric acid:lactic acid complex.[323] Equilibrium constants have been estimated for the formation of boric acid–lactic acid complexes.[324] Two types of complex were observed, with their deprotonated forms predominating at increased pH. Potentiometric titration studies have also been used to derive an equilibrium constant for formation of a 1:1 boric acid:lactic acid complex.[325] Electrical conductivity increases as a consequence of complex formation have also been observed for boric acid in the presence of α-(1,1)-hydroxy cyclic acids containing from four to eight carbon atoms.[16, 17, 326] Conductivity titrations and viscosity and cryoscopic measurements have indicated that boric acid forms 1:1 and 1:2 complexes with mandelic acid[327] and an equilibrium constant of $3{\cdot}02 \times 10^9$ has been obtained for formation of the 1:1 complex.[328] In other work it has been reported that boric acid may form a 1:1 complex[329] and ester[330] with stearic acid substituted by two to four hydroxyl groups, and the formation of a 1:1 complex has been supported by infra-red studies.[331] Boric acid has been shown to form a complex with malic acid in solution[332] and more recently the crystal structure of potassium boromalate monohydrate has been examined.[333]

Optical rotatory dispersion measurements at controlled pH have shown that boric acid forms a 1:1 complex with tartaric acid.[334] The equilibrium constant for its formation was determined and acid dissociation of the complex was found to occur above pH 4. The formation of boron-containing complexes from tartaric acid was also supported by phase diagrams for the systems sodium pentaborate–sodium bitartrate–water[335] and Na_2O–B_2O_3–tartaric acid–water[336] and by the behaviour of tartaric acid on titration in the presence of boric acid.[337] Conductance and polarimetric measurements have shown that in mixtures of sodium tartrate with sodium metaborate or borax, 1:1 complexes with a boron:tartrate ratio of 1:1 or above may form.[338] Evaporation of aqueous solutions of tartaric acid and boric acid has been used to form 1:1 and 2:1 borate:tartrate complex acids, and pH and conductivity measurements on the products were used to determine their dissociation constants.[339] The structure of the isomers of tartaric acid has been examined by electrical conductivity measurements in the presence of boric acid[340] and other conductivity and cryoscopic measurements have indicated that in aqueous solution boric acid forms both a 1:1 and a 1:2 borate:tartrate complex with the hydroxyl groups of fully ionized tartaric acid[341]; on dilution the boroditartrate dianion loses one molecule of tartaric acid. Solubility measurements for boric acid in the presence of tartaric acid have also shown that the acids interact in a 1:1 and 1:2 borate:tartrate ratio[342] and optical activity studies have confirmed the formation of complexes of this stoichiometry.[343] Stability constants for these complexes have been obtained from polarimetric measurements on the boric acid–tartrate system.[344] An anion-exchange method has been used to study the influence of pH on the nature of the boric acid–tartaric acid complexes[345], and it was reported that for increasing pH there is a change from the 1:2 to the 1:1 borate:tartrate complex anion, and from thence ionization of complexed tartaric acid increases with pH. In other studies of these several complexes equilibrium constants for their formation were obtained from pH, polarimetric and potentiometric measurements.[346] Borate–tartaric acid complexes have also been prepared by heating aqueous solutions of the components, and instability constants were obtained from potentiometric measurements on these products.[347] More recently rate constants for complex formation by boric acid with tartaric acid and the tartrate anion have been obtained by relaxation spectrometry using the temperature-jump method.[348, 349]

The several complexes formed by boric acid in association with different proportions of tartaric acid in varying ionization states have been prepared by evaporation[350] and precipitation[351] and their composition established by techniques including *X*-ray analysis[350], infra-red spectroscopy and thermogravimetry.[351] Previous thermographic study of the system boric acid–tartaric acid had indicated their interaction in a 1:1 ratio.[352] Other structural studies using infra-red spectroscopy and differential thermal analysis have confirmed that boromonotartrates and boroditartrates have respectively cyclic and spiro structures[353], and the same methods have been used to examine the structure of other borotartrates, including those of the alkali and alkaline-earth metals.[354, 355]

In preparative work borate complexes of both methyl and ethyl tartrate have been crystallized from the ester and boric acid in aqueous solution.[356] Amine salts of the 1:2 boric acid:tartaric acid complex have been obtained from aqueous solution[357] and from the anhydrous components.[358] Mixed manganoborotartrates of the alkali metals and ammonium have been reported[359], and the decomposition of some manganese borotartrates in aqueous solution has been studied.[360] Borotartrate complexes have also been prepared containing vanadium[349], iron[361] and copper[362], and stability constants for these metal borotartrates are reported. A complex barium borotartrate has been prepared from aqueous borate solutions[363] and its precipitation has been exploited for the detection of borate down to a concentration limit of 10 p.p.m. of boron.[364] Lanthanide salts of borotartrate complexes have also been prepared by precipitation from aqueous solution.[365]

Potentiometric titration results have demonstrated the formation of 1:1 and 1:2 boric acid: citric acid complexes[366], for which the respective dissociation constants were found to be 1×10^{-2} and 5×10^{-5}. The 1:2 complex was found to be favoured at low pH. More recently a complex borodicitric acid has been crystallized from an aqueous mixture of boric acid with citric acid.[367] Solubility studies on the system boric acid–citric acid–water have also confirmed the formation of 1:1 and 1:2 boric acid: citric acid complexes.[368] Salts of the trivalent 1:1 complex anion with alkali and other heavier metals[369], and lanthanides[370], have been prepared from aqueous solution. Amine salts of the pentavalent 1:2 borate:citrate complex have also been obtained by precipitation from aqueous solution and their structures were examined by thermographic methods.[371]

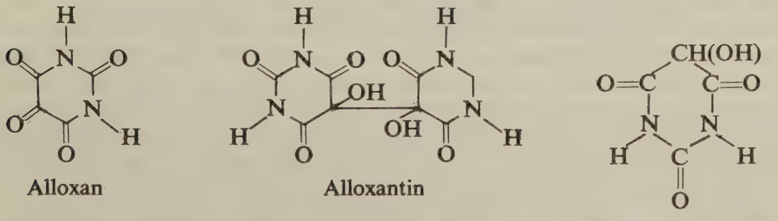
In an examination of the system sodium hydroxide–boric acid–trihydroxyglutaric acid–water a sodium salt of the divalent 2:1 borate:trihydroxyglutarate complex anion was prepared.[372] In other similar studies this salt and the sodium salt of a tetravalent 1:2 borate:trihydroxyglutarate complex anion were isolated.[373] Further work has confirmed the formation of these complex anions[374–376] and has shown that the formation of a 2:1 complex is favoured by a higher pH than that leading to the formation of the 1:2 complex. In a study of the borotrihydroxyglutarates of some alkaline-earth metals a 2:3 borate:trihydroxyglutarate complex has also been reported[377, 378] and a trivalent 1:1 complex borotrihydroxyglutarate salt of zinc and cadmium was also prepared.[377] Thermographic studies have confirmed the formation of the latter complex from boric acid and trihydroxyglutaric acid on evaporation[379], and from sodium borate and sodium trihydroxyglutarate on dry heating.[380] Dissociation studies have also shown that the complex borate anion persists in solution after the dissociation of the cadmium and mixed zinc and ammonium salts of the 1:1 borotrihydroxyglutarate anion.[381] A barium salt of the complex of boric acid with arabotrihydroxyglutaric acid has been precipitated from aqueous solution at alkaline pH[382], and lanthanide salts of the 1:1 borotrihydroxyglutarate anion have been prepared.[383]

Although thermographic studies of solid boric acid and mucic acid gave no evidence for complex formation[384], a barium salt of a trivalent 1:1 boric acid: mucic acid complex has been formed by precipitation from aqueous solution.[385] Other alkali-metal and alkaline-earth metal salts of this complex of general formula $3MO,B_2O_3,2C_6H_8O_4,nH_2O$ (M = bivalent metal) have also been precipitated from hot aqueous mixtures of metal salts, boric acid and mucic acid at alkaline pH.[386-388] A nickel boromucate of this type has also been precipitated from aqueous solution at alkaline pH[389], and calcium and strontium salts of galactaric acid have been obtained in the same way.[390] Mixed ammonium and cadmium salts of the pentavalent 4:3 boric acid: mucic acid complex anion have also been precipitated from aqueous solution.[391]

From early polarimetric studies it was recognized that with gluconic acid, as with the ionizable polyhydroxy compounds above, borate complex formation involved both the reaction of the borate anion with hydroxyl groups and the reaction of boric acid with the carboxylate anion.[37] It has been shown that calcium gluconate may be used in place of mannitol for the titrimetric determination of boric acid[392-394] and the formation of a 1:2 boric acid: gluconic acid complex was proposed.[394] Studies have been made of the dissociation of complex alkali-metal and alkaline-earth metal borogluconates in aqueous solution[395] and sodium borogluconate complexes have been prepared from aqueous solution.[396, 397] Di-, tri- and tetrabasic borogluconates were obtained at pH 5, 8–9 and 14, respectively.[397] Thermographic and spectroscopic studies have also been performed on mixed calcium and alkali-metal borogluconates of the general formula $M_2CaB_2C_{12}H_{22}O_{18},nH_2O$ (where M is the alkali metal) which were reported to be obtained as vitreous products from aqueous solution.[398, 399]

Nitrogen-containing Compounds

Some early tests on several nitrogen-containing organic compounds for formation of boric acid complexes used electrical conductivity measurements and showed that glycine has some tendency, albeit less than the corresponding hydroxy-acid, to form a borate complex, and that uric acid glycol also raised the conductivity of aqueous boric acid slightly.[400] Alloxan, alloxantin and hydroxybarbituric acid were amongst the compounds without effect on the electrical conductivity of boric acid (Fig. 2). Ultra-violet spectrophotometric work has indicated that boric acid may give a 1:1 complex with benzohydroxamic acid (Fig. 3) and an equilibrium constant $pK = 5{\cdot}7$ was reported for its formation.[401] The formation of a 2:1 boric acid: benzohydroxamic acid complex has also been reported from spectrophotometric measurements and chemical analysis of the isolated product.[402] Other studies have shown that boric acid forms a 1:1 chelate with salicylamide, salicylhydrazide and salicylhydroxamic acid (Fig. 4).[403] There is also evidence for the formation of a mixed borate complex from catechol and several *N*-alkylsalicylaldimines (Fig. 5).[404] Ultra-violet spectrophotometric work has indicated

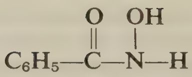


Alloxan

Alloxantin

Hydroxybarbituric acid

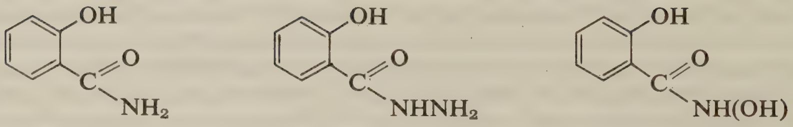
Fig. 2



$C_6H_5—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{\overset{\displaystyle OH}{|}}{N}—H$

Benzohydroxamic acid

Fig. 3

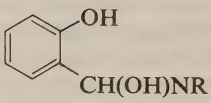


Salicylamide

Salicylhydrazide

Salicylhydroxamic acid

Fig. 4



N-alkylsalicylaldimine

Fig. 5

that borax forms a weak complex with the oxime of salicylaldehyde, and a formation constant of $(3{\cdot}0 \pm 0{\cdot}2) \times 10^{-3}$ was deduced.[405] More recently it has been reported that a tris-dimethylglyoxime complex of iron(II) containing two molecules of boric acid as a complex with the oxime hydroxyl groups may be prepared from a solution of boric acid, an iron(II) salt and dimethylglyoxime.[406, 407] Boric acid has also been reported to form a complex with its own triethanolamine ester, having the composition $B(OC_2H_4)_3$-$NB(OH)_3$.[408]

Heteropolyacids and Inorganic Ligands

Compounds formed by boric acid with heteropolyacids have received a full treatment in Section 13 of this volume. Attention has been given to the structure of the molybdate anion in coordination complexes[409] and the structures of heteropolyacids themselves have been reviewed.[62] The reaction of boromolybdate and borotungstate anions, $BM_{11}O_{39}^{m-}$ (where M is tungsten or molybdenum and *m* is an integer) with transition metal (Z) ions in aqueous solution has been found to give heteropolyanions of stoichiometry $BZM_{11}O_{40}^{n-}$ (where *n* is an integer) containing tetrahedrally coordinated boron.[410] Tungsten complexes of this type were found to be more stable than those containing molybdenum, and the structure of other complex transition metal borotungstate anions was also classified in this work.[410]

The effect of pH and the B:W ratio of the reactants upon the nature of the complex borotungstate formed from the anodic acidification of a boric acid–sodium paratungstate mixture has been studied.[411] Sodium borotungstates having B:W ratios of 1:12, 1:14, 1:13 and 1:15 have been prepared by this method[412] and a crystalline sodium molybdoborate (B:Mo = 1:12) has also been prepared in the same way.[413] The pentapotassium salt of tungstoboric acid has been prepared, and thermographic study has indicated that the fully hydrated salt has the formula $K_5(BW_{12}O_{40}),18H_2O$.[414] Differential thermal analysis and *X*-ray diffraction methods have also been used to determine the formulae of 12-tungstoboric acid and its ammonium salt.[415] The structure of 12-tungstoboric acid has also been elucidated by E.S.R. studies of the transformation of hydroxonium ions in the lattice to protons during dehydration.[416] In aqueous solution 12-tungstoboric acid has been found to undergo a single acid dissociation as a strong pentabasic acid.[417] This result has been confirmed by other neutralization work[418, 419], polarographic studies[420] and proton N.M.R. investigations.[421] More recently the basicity of borotungstic, borotungstovanadic and boromolybdotungstic acids has been studied.[422] There was evidence for two neutralization steps in amphoteric solvents, whereas the acids behaved as tribasic acids in protogenic solvents. The decomposition of 12-borotungstic acid during its neutralization with sodium hydroxide has been the subject of a cryometric study[423] and the stability of this acid on dilution and neutralization has been examined by polarography.[420] In other work alkali metal salts of 12-borotungstic acid showed no neutralization reaction with sodium hydroxide but decomposed in the presence of a twenty-seven fold molar excess of the hydroxide.[424] Other polarographic studies of the reduction of 12-tungstoboric acid have shown that the acid may form reduced species with 6, 7, 8, 12 and 18 electrons transferred into the acid anion.[425]

It has been reported that borotungstic and boromolybdic acids may be prepared as crystals from the reaction of boric acid with molybdic or tungstic acid in aqueous solution.[426] The cæsium[427] and rubidium[427, 428] salts of a mixed borotungstovanadic acid have also been precipitated from aqueous solution, and the rubidium and cæsium salts of the complex borotungstovanadic acid $H_9(B(W_2O_7)_5V_2O_6)$, precipitated from acid solution, have been found to have a basicity of three.[429] A rubidium salt has also been prepared from 12-tungstoboric acid and shown by dehydration studies to have the formula $Rb_5(BW_{12}O_{40}),nH_2O$ where *n* may be 18, 11, 7·5 or 2·5.[430] The structure of an analogous cæsium salt has been confirmed by *X*-ray methods.[431] Crystalline ammonium 12-borotungstate has been prepared from the reaction of boric acid with ammonium tungstate ($(NH_4)_6(H_2W_{12}O_{40}),12H_2O$)[432] and infra-red assignments have been made for ammonium 12-tungstoborate.[433] The preparation of sodium borotungstate ($Na_5H_4(B(W_2O_7)_6)$) from boric acid and sodium tungstate (Na_2WO_4) has also been described.[434, 435] The potassium salt of 12-tungstoboric acid has also been used to precipitate bis(benzoylacetonyl)-beryllium(II) from solution in a benzene–ethanol mixture.[436]

A study of the physicochemical properties of the borotungstates of barium, cobalt and copper has been reported[437] and the solubility and hydration of cobalt and copper borotungstates has been examined.[438] In other work equilibria in the system copper borotungstate–water have been examined over a range of temperatures[439], and cadmium borotungstate has been prepared by an exchange reaction from barium borotungstate.[440] Magnetic measurements and stability studies have also been performed on borotungstate anions containing divalent copper and manganese, and trivalent manganese.[441]

A study of component solubilities in the system boric acid–ammonium vanadate–water has been reported and gave evidence for compound formation.[442] An examination of the steam volatility of boric acid in the presence of other salts has also been interpreted as evidence for the existence of complex borophosphoric and boroarsenic acids in solution.[443] A stable chromium(II) compound of composition $CrXOH,H_3BO_3$ ($X = Cl$, Br or I) has been reported to be formed as a precipitate from aqueous solution by the reaction of chromous chloride with boric acid in the presence of calcium salts.[444] *X*-ray study of the product showed a tetragonal symmetry, and although it may be formulated as containing the tetrahydroxyborate anion its composition has not received further attention. A related zirconium(II) compound of composition $H_3BO_3ZrOHCl,3{\cdot}5H_2O$ has also been reported to be precipitated from an aqueous mixture of zirconium oxychloride and boric acid after heating.[445]

Physical Properties of Complex Borate Anions and their Salts

Ionization Effects

ACIDITY AND ELECTRICAL CONDUCTIVITY

It has been established that in aqueous solution the action of boric acid as a Lewis acid (equation 3 above) is encouraged by the involvement of the resulting tetrahydroxyborate anion in complex formation. Investigations in which this effect has been exploited to give quantitative results from potentiometric titration or pH measurements are treated in detail in previous sections under the heading of the appropriate complexing agent. Hydrogen-ion concentrations have been recorded for boric acid in the presence of hexose sugars[132] and potentiometric titration has been used to study complexation

Table V.—Enhancement of the Conductivity of Boric Acid Solutions by Various Additives.[9]

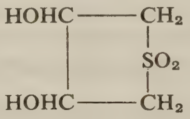
Substance	Conc.	*Δ*
Polyols		
Glycol	0·5 *M*	0
Glycerol	0·5 *M*	+ 9
Erythritol	0·5 *M*	+ 72
Adonitol	0·5 *M*	+ 90
Arabitol	0·5 *M*	+357
Xylitol	0·5 *M*	+625
Mannitol	0·5 *M*	+685
Dulcitol	0·5 *M*	+717
Sorbitol	0·5 *M*	+794
Cyclic Glycols		
Cyclopentane-1,2-diol (*cis*)	0·5 *M*	149
1-Methylcyclopentane-1,2-diol (*cis*)	0·5 *M*	114
Cyclopentane-1,2-diol (*trans*)	0·5 *M*	neg.
1-Methylcyclopentane-1,2-diol (*trans*)	0·5 *M*	neg.
α-Mannitan	0·5 *M*	776
N-Ethyl-*meso*-tartrimide	0·5 *M*	702
N-Methyl-*dextro*-tartrimide	0·5 *M*	neg.
Indane-1,2-diol (*cis*)	$\frac{1}{7}$ *M*	63
Indane-1,2-diol (*trans*)	$\frac{1}{7}$ *M*	neg.
Tetramethylenesulfone-2,3-diol (*cis*)	0·5 *M*	494
Tetramethylenesulfone-2,3-diol (*trans*)	0·5 *M*	neg.
2-Methyl-tetramethylenesulfone-2,3-diol (*cis*)	0·5 *M*	1096
2-Methyl-tetramethylenesulfone-2,3-diol (*trans*)	0·5 *M*	neg.
1,4-Dimethyl-tetramethylenesulfone-2,3-diol (*cis*)	0·5 *M*	1458
1,4-Dimethyl-tetramethylenesulfone-2,3-diol (*trans*)	0·5 *M*	neg.
These sulfonediols are of the type:		
		
Phenols		
1,2-Dihydroxybenzene (catechol)	1 *M*	681
1,2,3-Trihydroxybenzene (pyrogallol)	1 *M*	909
1,2,4-Trihydroxybenzene (hydroxyhydroquinone)	0·5 *M*	322
1,2-Dihydroxynaphthalene	$\frac{1}{32}$ *M*	65
2,3-Dihydroxynaphthalene	$\frac{1}{200}$ *M*	92
3,4-Dihydroxybenzoic (protocatechuic) acid	$\frac{1}{32}$ *M*	68·7
3,4,5-Trihydroxybenzoic (gallic) acid	$\frac{1}{32}$ *M*	41·1
1,3-Dihydroxybenzene (resorcinol)	0·5 *M*	neg.
1,4-Dihydroxybenzene (hydroquinone)	0·5 *M*	neg.
1,3,5-Trihydroxybenzene (phloroglucinol)	0·5 *M*	neg.
Hydroxy-Acids		
$CH_2OH\cdot COOH$	0·5 *M*	441
$CH_3CHOH\cdot COOH$	0·5 *M*	14,213
$(CH_3)_2COH\cdot COOH$	0·5 *M*	41,307
$C_6H_5CHOH\cdot COOH$	0·5 *M*	21,500
$(C_6H_5)_2COH\cdot COOH$	$\frac{1}{128}$ *M*	555
$C_6H_{12}CHOH\cdot COOH$	$\frac{1}{128}$ *M*	416
$CH_2OH\ CHOH\cdot COOH$	0·5 *M*	21,700
$CH_2OH(CHOH)_4COOH$	0·5 *M*	21,636
CH_2OHCH_2COOH	0·5 *M*	neg.
$C_6H_5CHOHCH_2COOH$	0·5 *M*	neg.
$CCl_3CHOHCH_2COOH$	0·5 *M*	neg.
$CH_2CHOHCH_2CH_2COOH$	0·5 *M*	neg.
Salicylic acid	$\frac{1}{64}$ *M*	1264
2,4-Dihydroxybenzoic acid	$\frac{1}{64}$ *M*	1501
2,4,5-Trihydroxybenzoic acid	$\frac{1}{64}$ *M*	1102

Table V.—continued

Substance	Conc.	Δ
2-Hydroxycyclopentanecarboxylic acid (*cis*)	$\frac{1}{8}$ M	96
2-Hydroxycyclopentanecarboxylic acid (*trans*)	$\frac{1}{8}$ M	neg.
5-Methyl-2-hydroxycyclopentanecarboxylic acid (*cis*)	$\frac{1}{8}$ M	89
5-Methyl-2-hydroxycyclopentanecarboxylic acid (*trans*)	$\frac{1}{8}$ M	neg.
Borneolcarboxylic acid (*cis*)	$\frac{1}{64}$ M	530
Borneolcarboxylic acid (*trans*)	$\frac{1}{64}$ M	neg.

by these compounds, as well as glycerol and ethylene glycol[134,140], and the isopropylidene derivatives of mannitol and glucose.[446] Potentiometric titration measurements have also been made on boric acid in the presence of polyphenols and organic acids[253] and nucleoside complexants.[193] The increase in electrical conductance which also accompanies ionization of the complex boron-containing acids ($HBP(OH)_2$ or HBP_2) has been recorded for a range of complexing agents[9] (Table V), and some earlier work relating this effect to the configuration of the complexing agent has also been summarized.[310] In some other early work measured increases in the conductivity of boric acid in the presence of several glycols[447] were correlated with their ability to form condensates with acetone.[447,448] Attention has also been given to some hydroxy carboxylic acids which caused a decrease in the conductivity of boric acid and did not form complexes.[449] A condensation interaction of the acid with boric acid was proposed as responsible for this decrease in conductivity.

For the boric acid–complexant system the effect of temperature upon electrical conductivity has been reported only with citric acid[450], and the temperature coefficient of conductivity was found to be small. Precise conductivity measurements have been made upon boric acid in the presence of hexose and pentose sugars[147,451,452], polyhydric alcohols[66,453,454,455], carbohydrates[455] and bicyclic diols.[456] Attention has been given to the influence of the configuration of carbohydrates[176] and both sugars and polyhydric alcohols[457,458] upon these measurements. A number of conductivity studies have been reported for boric acid in the presence of α-hydroxy carboxylic acids[309,319,326,459–463] and α-ketocarboxylic acids[311,312,313], and measurements have also been made in the presence of dibasic acids[320] and glyoxal.[294] Conductivity values have also been recorded for boric acid with phenols and hydroxy naphthalenes[252,264,464–6] as well as with saligenin[290], salicylic acid[278] and para-aminosalicylic acid.[285] The complexation of boric acid by urea has also been studied, and conductivity measurements were reported.[400] In other electrical conductivity studies the effect of boric acid upon the specific resistivity of ethylene glycol in the presence of ammonia has been determined.[467]

TRANSPORT PROPERTIES

The formation of complex anions from boric acid in the presence of suitable polyhydroxy organic compounds has a significant influence on their transport properties, as evidenced by chromatography and electrophoresis experiments, and the study of related effects. Borate-containing solutions have been used for the selective elution of complexing sugars after their absorption on carbon[10,11] and strong-base anion-exchange resins.[468,469] More recently a complex-forming boron group, analogous to that in the tetrahydroxyborate anion, has been incorporated in a methacrylic acid polymer and used to assess the complexing ability of some nucleotides[199,200] and sugars.[188] Transport effects have been recorded in a study of the 12-borotungstate anion by paper chromatography[419] and have been exploited for the study of amylose–borate interactions by gel filtration.[186] The chromatographic separation of some tritium-labelled ester lipids on a mixed silicic acid–boric acid column has also been used to effect their detritylation.[470] The exploitation of borate complexes in thin layer chromatography has apparently been confined to the separation of benzyl alcohol derivatives and pyridoxol on silica gel impregnated by boric acid.[218] Reviews have

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appeared on the effect of complexation by boric acid upon the zone electrophoresis[8] and paper electrophoresis[7] of carbohydrates, and the effect of boric acid on the paper electrophoresis of carbohydrates[182, 471] and polyhydric alcohols[472] has also been examined more recently. The behaviour of proteins on gel electrophoresis as borate complexes has also been examined.[473] Boric acid complexes exhibit a measurable ionophoretic mobility and this effect has been examined for a range of complexing carbohydrates[125, 474–6], disaccharides[477], sugars[478] and cyclitols.[77] The formation of complex anions by boric acid with lactic and oxalic acids has also been studied by electrodialysis using an anion-exchange membrane.[321]

ION EXCHANGE

The ion exchange behaviour of boric acid upon complex formation has been examined for several complexants, particularly since this property offers the possibility of making a quantitative estimate of the extent of complex formation by a relatively straightforward method. In a study of the anion-exchange properties of boric acid in the presence of glycols, complexation constants were obtained by applying an elution equation derived from the plate theory of ion-exchange chromatography.[67] Several complexing sugars have been absorbed by strong-base ion-exchange resins as borate complexes formed in sodium borate solution[468] and were separated on subsequent elution with this same salt[468] or boric acid solutions.[469] Ion-exchange chromatography in the presence of boric acid has also been used to separate a mixture of ribosides.[198] The ion exchange properties of complex anions present in the system boric acid–tartaric acid–water have been studied[345] and the system boric acid–lactic acid–water has also been examined by this technique.[323] The anion-exchange behaviour of boric acid in the presence of oxalic acid has been shown to be consistent with the formation of a 1 : 1 complex anion[479], and the absorption of boric acid by an anion-exchange resin previously saturated with the anions of other hydroxy di- and mono-carboxylic acids has been studied.[480] It was concluded that boron was absorbed not only as a discrete complex anion but also in a bridging position between adjacent complexant molecules, and as a condensed species.[480] The effect of complexing agents on the retention of boric acid by anion-exchange resins and other absorbents has received attention in other work.[481] The anion-exchange behaviour of boric acid in the presence of glycerol[86, 91, 92], mannitol[165], catechol[251] and tartaric acid[345] has been examined, and the formation of a complex anion from boric acid and gluconic acid has been demonstrated by ion exchange.[482]

Solution Properties

SOLUBILITY MEASUREMENTS

Solubility measurements on boric acid and borates in the presence of water and a complexing agent have been performed in a range of instances to investigate the formation and composition of anionic complexes. The solubility of such species in water has been studied in other cases to enhance the dissolution or effect the extraction of suitable organic complexants by water. Similarly the solubility of particular borate complexes in water-immiscible solvents has allowed the extraction of borate and associated ions from aqueous solution, and in a few instances quantitative studies of borate complexation have been made by this solvent extraction method. More recently the decomposition of some borate ores has been effected as a consequence of the complexation of boric acid therefrom during their dissolution by some hydroxy-carboxylic acids.

Alkali-metal salts of several complex borate anions have been isolated from the components in aqueous solution, and metal salts of boric acid–heteropolyacid complexes have been prepared by crystallization from concentrated aqueous solution. Anionic complexes of boric acid with pentaerythritol and hydroxycarboxylic acids show a low aqueous solubility in association with alkaline-earth or the later transition metals as gegenions and this has been exploited in the gravimetric determination of boron, e.g. as barium borotartrate.

Solubility studies have been performed on the system sodium hydroxide–boric acid–water–trihydroxyglutaric acid and led to the isolation of two complex salts.[373] Solubility measurements have also been made on the system boric acid–tartaric acid–water[483] and solubility data have been recorded for boric acid in the presence of the sugars mannitol[263] and sorbitol[139] and the complexing alcohols *cis*-tetrahydronaphthalene-1,2-diol[263] and 1,3-butanediol.[484] In measurements of the aqueous solubility of copper borotungstate, several hydrates were isolated[439], and a phase diagram showing the formation of lithium borotungstate in the system Li^+–$K^+WO_4^{2-}$–BO_2^- has been obtained from the cooling curves of related components.[485] The solubility of riboflavin in water has been shown to be increased by the presence of boric acid[212], and in separate studies a complex has been formed.[211] The system boric acid–glycerol–water has also been found to effect the solubilization of several alkaloids[486], and the presence of boric acid has also been reported to enhance the extraction of mannose derivatives from wood cellulose.[191]

The solubility of boric acid complexes in organic solvents has been exploited in the solvent extraction of boric acid from aqueous solution; alkyl salicylic acids have been reported to be useful solvent extractants for aqueous borate[487,488], whilst aromatic alcohols[489–491], saturated aliphatic diols and triols[492–494] and alkyl catechols[493] have been patented for use under more alkaline conditions. The extraction of aqueous boric acid by alkyl catechols has been described[495], and comparative extraction studies of various 1,3-diols amongst themselves[496], and with diketones and hydroxyketones[497] have been reported. A complex of boric acid with salicylic acid has been extracted into tributyl phosphate for analysis[498], whilst aqueous boric acid at pH 2 has been extracted into branched-chain, five-carbon diols and triols for the same purpose.[499] In studies of inorganic complexes it has been shown that tungstoboric acid may be extracted from acid solution by butanol[500] and boromolybdotungstic acid has been extracted quantitatively from aqueous acid solution by solvents, including butanol and benzene.[501] Studies have also been made of the dissolution of natural borate minerals in dicarboxylic and hydroxydicarboxylic acids.[502,503]

Among the complexes of boric acid with polyhydroxy compounds, salts obtained from catechol complexes precipitate or crystallize most readily from an aqueous solution of the components. Salts of 1:2 boric acid:catechol complexes have been crystallized in several cases from aqueous solution[28,29,31,40,234,356], and the relative solubility of mono- and di-catechol borate salts has been found to depend upon the gegenion.[231] Alkali-metal and amine salts of the dicatechol borate anion have been crystallized from concentrated solutions of the appropriate reagents[25], and its thallium and lower alkali-metal salts have been found to have a low aqueous solubility.[233] An amine salt of a diphenoxy catechol borate has also been obtained by crystallization from an aqueous solution of boric acid and catechol.[229] Glycerol borate salts, brought down from aqueous solution by ethanol, were found to be rapidly hydrolyzed by water[504], but a cadmium salt of this anion has been reported to have only a low solubility in water at alkaline pH.[505] Salts of boric acid and pinacol have been crystallized from an aqueous solution of the components[54], and pentaerythritol has been found to give a polymeric sodium salt in this way.[54] The potassium salts of boric acid complexes with methyl and ethyl tartrates have been obtained from aqueous solution[356], and salts of a boric acid complex with salicylic acid have been found to have a low aqueous solubility.[234,287] Boric acid salts of low aqueous solubility have also been obtained from vicinal cyclopentane- and cyclohexane-diols[31] and from scyllitol.[119] A 1:1 boric acid:mannitol complex has been obtained from aqueous solution[173], and similar complexes of boric acid with mannitol and glucose have been obtained from the components in acetone.[174] A salt of a boric acid–ascorbic acid complex has been brought down from alcoholic solution by adding an alkali-metal hydroxide in aqueous solution[209], and cobalt tetraamine diboroascorbate has been obtained from aqueous solution.[208] A monobasic complex of boric acid with the cymarose glycoside of the steroid strophanthidin[195], and a monoborate complex of the antibiotic erythromycin[224] have also been obtained from the components in aqueous solution, and an iron–dimethyl glyoxime chelate containing complexed boric acid has been crystallized from aqueous solution.[407]

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Cadmium borotungstate has been obtained from aqueous solution only after concentration by evaporation[440] and borotungstic and boromolybdic acids[426] and their salts[432] have also been crystallized from solution only after concentration. Some metal and amine salts of borotungstovanadic acid have, however, been precipitated from aqueous solution.[428] Syntheses have shown that the alkaline-earth[99, 100], zinc and cadmium[101] and nickel[102] salts of the complex anion from boric acid and pentaerythritol have a low solubility in water. The same observation has been made for salts of the complex anion from boric acid and tartaric acid in association both with ions of alkaline-earth metals[364, 378, 506], and with alkaline-earth metals[377, 507, 508] and zinc[509] in combination with ammonia, hexyl- and heptyl-amines[357] and some lanthanides.[365] Preparative work has also shown that the alkali-metal[372, 374] and alkaline-earth metal[382, 510] salts of the complex of boric acid with trihydroxyglutaric acid have a low solubility in water. The borocitrates of some quaternary amines[511], alkali and alkaline-earth metals[369], later transition metals[369] and lanthanum[370] have also been formed as precipitates from aqueous solution. Other studies have shown a low aqueous solubility for a range of salts of anionic complexes formed by boric acid with mucic acid[387, 389, 391] and gluconic acid[396, 398, 399], as well as with the sugar acids galactaric acid[390] and saccharic acid.[512]

VISCOSITY AND GELATION

An increase in the viscosity of aqueous boric acid has been observed upon complex formation with several organic reagents, and is generally a consequence of hydrogen bonding and borate complexation acting together to give a cross-linked structure, which may form a gel in extreme cases. Viscosity studies appear to have been confined mainly to compounds with relatively high equilibrium constants for complex formation, but with suitable reagents gel formation may occur with stoichiometric or lower amounts of complexant. The gelation of boric acid by many polysaccharides has been examined in detail[60] and viscosity studies using gums and mucilages have been included in a general review of complex formation.[61, 183] Gel formation is an established feature of complex formation from boric acid with polyvinyl alcohol[105] and starch, and some comparative studies have been made upon dextrins.[513] Early work was concerned with carob-seed gum, with which complexation of the tetrahydroxyborate anion leading to gel formation is particularly marked, even at low concentrations of borax, its precursor.[514, 515] More recently gelation in the guanosine–boric acid–water system has been studied and shown to be due to the formation of a 2:1 guanosine: boric acid chelate held in a hydrogen-bonded network.[194] Gelation in this system was found to be inhibited by urea.[194] In an examination of the viscosity of boric acid in the presence of other polysaccharides, including mannan, galactomannan and polymannuronic acid, gelation was found to be inhibited by lower molecular-weight complexing agents and by acid.[183] In other work it has been reported that borax reduces the viscosity of alginate solutions[516], and pectin has been found to accomplish the gelation of boric acid only after its conversion into a glycerol ester.[517] The influence of borates upon gel formation from gelatin has also been examined.[518] Volume changes on complex formation from boric acid may be formally related to viscosity effects and have been exploited to study the formation of boric acid complexes by mannitol and sorbitol.[157] Measurements have also been made of the viscosity of boric acid in the presence of polyvinyl alcohol,[105] trihydroxyglutaric acid[519] and tartaric acid[342], and have been used in a study of the formation of a borate complex by mandelic acid.[327]

Thermodynamic Properties

Equilibrium constants measured for the formation of borate complexes are dealt with earlier in this section under the appropriate reactants. From potentiometric studies of the system boric acid–mannitol–water thermodynamic functions ΔH, ΔG° and ΔS° were determined for the complexation reactions leading to 1:1 and 2:1 mannitol: boric acid complexes.[171] Both reactions were found to be exothermic, but enthalpy changes were small. The free-energy change on complexation showed no appreciable temperature dependence and the corresponding entropy changes were found to be positive, so that the entropy change accompanying complexation represents the main contribution to the associated free-energy change. This behaviour has also been found in a similar study of the complexation of boric acid by pyrocatechol.[245] In other work the same functions were also obtained for the complexation of boric acid by a range of 1,2- and 1,3-dihydric alcohols by using a pH method to study the complexation reaction at several temperatures.[79] The method has also been used to derive the same thermodynamic data for the chelation of boric acid by some hexose sugars.[137] Comparison of these results and earlier work[171] is possible for complexation by mannitol, and here the later results[79] show fair agreement only for free-energy changes. Calorimetric measurements have been made of the heat of neutralization of boric acid in the presence of mannitol and catechol[169], but studies of this effect are complicated by the formation and interconversion of the two complex acids ($HBP(OH)_2$ and HBP_2). Thermodynamic studies of complex formation by boric acid with inorganic species are apparently confined to measurements of the heat of reaction of some alkali-metal borotungstates with sodium hydroxide.[424]

Optical and Spectroscopic Properties

OPTICAL ROTATION

The change in optical rotation of suitable organic compounds in the presence of boric acid or borates was one of the earliest observed effects of complex formation, but such changes do not always accompany or originate from complex formation. Optical activity measurements have been performed upon mixed systems and the complexes themselves, and show that changes in optical rotation can arise from the influence of boric acid on the organic complexant and the creation of a new asymmetric centre on complex formation. The action of boric acid in acid–base catalysis of sugar mutarotation is particularly significant, and it has also been shown that unsymmetrical substitution in a complexant forming a bis-diol borate can lead to an asymmetric product.[27] Although it was initially suggested that asymmetry was located at the oxygen atom of the complex[23] it has been recognized that four-coordinate boron may be an asymmetric centre in a spiran (BP_2^-) complex.[27, 520, 521] It follows that a 1:1 complex formed from boric acid has no new asymmetric centre.

The influence of boric acid upon the optical rotation of mannitol has been determined[4], and in other work optical activity measurements have given evidence for the formation of two complex ions by boric acid with both sorbitol and mannitol[522], with a maximum optical activity for the compound having the greatest proportion of boric acid.[523] The effect of boric acid upon the specific rotation of some partially methylated derivatives of mannitol has also been examined.[524] Optical activity determinations have been made upon some aldose sugars in the presence of borax[525] and the specific rotation of lactose has been found to be increased by the addition of boric acid.[526] The effect of boric acid on the rotatory power of ether sugars, including maltose, levulose, glucose and galactose, has also been investigated.[527] Other studies of the effect of boric acid and borax on the degree of rotation of several aldohexose and aldopentose sugars showed a relatively smaller effect for boric acid, compared with borax, whilst the latter was found to decrease the angle of rotation of some monosaccharides and have little effect upon disaccharides.[127] In a related study of some sugars and tartaric acid, mannitol and glucose showed a greater tendency to complex with borax than boric acid.[37] In other studies of the optical rotation of sugars and glucose the concentration of borax causing the maximum deviation in the optical rotation of glucose was determined, and it was reported that boric acid was without effect on the optical rotation of glucose.[129] In later work it was found that boric acid, at a suitable concentration, caused a small reduction in the specific rotation of glucose[177], and the optical activity of glucose has been found to decrease in the presence of borax, particularly at alkaline pH.[178] The influence of borax upon the specific rotation of several ketohexoses, hexitols and glucose has also been examined at varying sugar:borax compositions.[528] Optical activity and complexation were correlated to show that glucose forms at least a diglucose borate and a mono-glucose borate[528], and in other work the optical rotation of mixtures of borax and phenyl-β-D-glucopyranoside has been studied.[179] Boric acid has been found to increase the specific rotation of calcium gluconate[529], and an examination of the effect of boric acid and borax upon the optical rotation of gluconates and saccharates has been reported to confirm that formation of a borate complex is an ionic reaction.[530]

Several studies have been made of the optical rotation of mixtures of boric and tartaric acids[531–535], and these measurements have been interpreted as confirming the formation of a compound which gives complex ions in solution.[536] The effect of increasing pH upon the system has been recorded[537] and optical rotation effects have been used to probe the composition of complexation products from boric and tartaric acids.[338, 343, 538] The effect of boric acid upon the optical rotation of tartaric acid has also been used for the polarimetric determination of boric acid.[539, 540] Optical rotation measurements have revealed the formation of a 2:1 boric acid: tartaric acid complex in acid solution[541], and optical rotation has been used as a contribution to the calculation of equilibrium constants for complex formation between the two acids.[334] Polarimetric measurements have also been made as part of a detailed quantitative study of the boric acid–tartaric acid system[346] and have been used to calculate equilibrium constants for complex formation.[344] The effect of boric acid upon the optical rotation of lactic[542] and malic acids[543] has been studied, and optical isomers of 1:2 boric acid–salicylic acid complexes have been separated and studied.[544, 6] In other work the influence of boric acid upon the optical rotation of lactoflavin[213] and ascorbic acid[210] has been examined. The mixed enantiomers of a complex of boric acid with catechol have also been isolated in varying proportions as their brucine and strychnine salts.[545]

ULTRA-VIOLET AND VISIBLE SPECTROSCOPY

The ultra-violet absorption spectrum, in ethanol, has been determined for complexes of boric acid with pyrocatechol and was interpreted as supporting the formation of 3:1 and 2:1 catechol: boric acid complexes in the presence of pyridine.[230] Visible spectra have also been recorded for boric acid on complex formation with nitrocatechols.[242] In other work formation constants for complexes of boric acid with 3,4-dihydroxy benzaldehyde and several other aromatic compounds have been obtained by ultra-violet spectroscopy.[251] The ultra-violet absorption of complexes of boric acid with salicylic acid has been examined and the observed shift to longer wavelengths in comparison with mixtures of the components was attributed to hydrogen bonding.[546] Complex formation by boric acid with other aromatic compounds has been studied by a differential spectrophotometric technique[547], and with catechol derivatives their colour formation with boric acid has been exploited as an analytical procedure.[237]

In the colorimetric determination of carbohydrates it was found that boric acid slightly lowered the visible absorption of aldose sugars at acid pH in the presence of phenol, and this may be due to complexation of an enol form of the sugar.[548] The complexation of boric acid by ethylene glycol, glycerol, mannitol and sorbitol has been studied by spectrophotometry, and ionization constants of the complexes were obtained from hydrogen-ion measurements in this way, using a reference acid, and dinitrophenol as an acid-base indicator.[70] The ultra-violet and visible spectra of complexes of boric acid with salicylic acid have been examined[288], and bathochromic shifts observed in the ultra-violet spectrum of *p*-aminosalicylic acid in the presence of boric acid may be a consequence of complex formation.[281] Ultra-violet spectroscopy has been reported to show complex formation from boric acid and salicylaldoxime[405] and spectrophotometric studies have also been made of the formation of a 1:1 chelate complex by boric acid with salicylamide, salicylhydrazide and salicylhydroxamic acid[403], and of the complexation of boric acid by benzohydroxamic acid.[402] Visible absorption studies have been made of the complexation of boric acid by naphthoquinone[277] and anthraquinone[271, 274, 277] and several derivatives of the latter; in particular alizarin[271] and alizarin-S.[271, 274] Anthraquinone derivatives have also been used for the colorimetric determination of boric acid.[549] Boric acid has been found to give a large hypsochromic shift in the ultra-violet spectrum of aqueous 4,5-dihydroxy-2,7-naphthalene disulphonic acid at pH 6·5–10[550] and a *p*-nitrophenylazoderivative of this compound has been used for the colorimetric determination of boric acid.[270] The visible absorption of a chelate complex of boric acid with fluorone has been recorded[305], and spectrophotometric studies have been made of coloured complexes of boric acid with flavones, flavonols and chalcones in the presence of oxalic acid.[222, 277] Boric acid has also been observed to produce a bathochromic shift in the spectrum of flavones having adjacent hydroxyl groups[223], and has been found to form a coloured reaction product with the flavone quercitin.[221] The colorimetric determination of boric acid on complexation with curcumin at acid pH is an established procedure.

The visible absorption spectrum of rosocyanin, the complex product, has been studied[300], and ultra-violet absorption spectroscopy has been used to determine the formation[296] and dissociation[302] constants for rosocyanin. It has been observed that there is an interference in this colour reaction by the presence of other complexing agents.[303] The ultra-violet spectrum of rubrocurcumin, the complex formed from boric acid, curcumin and oxalic acid has also been examined.[300]

FLUORESCENCE, LUMINESCENCE AND PHOSPHORESCENCE EFFECTS

A study has been made of the effect of substituents upon the fluorescence of a 1:1 complex of boric acid with some esters of salicylic acid[551], and the fluorescent reactions of boric acid with both acetylsalicylic acid and salicylaldehyde[552] and salicylic acid have been examined.[553] The fluorescent reaction of boric acid with some *o*-hydroxycarbonyl compounds in concentrated sulphuric acid has also been studied[554–557], and applied to the detection of boric acid using resacetophenone.[558, 559] Metal and amine salts of a complex of boric acid with catechol have also shown phosphorescence after ultraviolet excitation[234]; the fluorescent emission of a 1:1 complex of boric acid with benzoin has also been examined.[560]

The luminescent properties of a boric acid phosphor activated by yohimbine have been studied[561] and measurements of phosphorescent emission lifetimes have been used to give formation constants for complexes of boric acid with benzoylacetone.[562]

INFRA-RED AND RAMAN SPECTROSCOPY

Infra-red spectra have been recorded for salts of the boric acid complex of the sugar xylitol[142], and Raman spectroscopy of the aqueous borate anion in the presence of mannitol[166], and several 1,2- and 1,3-dihydric alcohols[69], has confirmed the formation of chelate complexes with a 1:1 and 1:2 boric acid:complexant ratio. In other work with an aliphatic dihydric alcohol the complexation and esterification of boric acid by 2,3-dimethyl-2,3-butanediol has been studied by infra-red spectroscopy of the components[75] and the product on their evaporation.[563] Infra-red measurements on boric acid and lactic acid in aqueous solution have been used to estimate stability constants for the appropriate complexes[324], and the structures of metal salts of boric acid complexes from lactic and tartaric acids have been examined by infra-red spectroscopy.[564] The complexation of boric acid by hydroxy-carboxylic acids, including malic and glycolic acids[565] and hydroxy-stearic acids[331] has been examined by infra-red spectroscopy. Stability constants have been estimated, from infra-red studies, for the complexation of boric acid by the salicylate anion.[283] Infra-red spectra have also been recorded for rosocyanin, the complex of boric acid with curcumin[301], and ammonium 12-tungstoborate.[433]

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The general effects that complex formation with boric acid has upon the proton N.M.R. spectra of sugars have been outlined[78] and the technique has been used to study the structure of borate complexes formed from some 5-membered-ring vicinal dihydric alcohols[78] and from scyllitol[120], and to obtain a complexation rate-constant in the latter case. Structural information obtained from studies of carbohydrates by high-resolution proton N.M.R. has also been discussed in relation to the complexation of borate.[566] Proton N.M.R. has been used to invesigate the structure of a borate complex formed by the yeast mannan, *Trichosporon aculeatum* mannan[567], and has been applied to determine the formula and basicity of tungstoboric acid.[421] The formation of a complex by boric acid with glucose has also been examined by the combination of proton and ^{11}B N.M.R. spectroscopy.[138] More recently the changes occurring in ^{13}C N.M.R. spectra of complexing agents in the presence of the tetrahydroxyborate anion have been examined, and spectra have been obtained for a range of free carbohydrates, polyhydric alcohols and their borate complexes.[568–570] Besides giving information on the structure of the complexes and the conformation of the complexant therein, in some cases it has also been found that the spectra may be used to estimate the extent of complexation.[568, 569]

Chemical Properties

The reactions of borate complexes have not been examined in any diversity. They are largely those of the complexant and reflect the effect of complexation thereupon. The chemical properties of complexes are treated here in so far as they may be separated from the chemical effects of complexation. The latter have received attention earlier, when there is emphasis on their exploitation to study the complexation of borate by a particular species.

REDUCTION AND OXIDATION

It has generally been observed that complex formation with boric acid decreases the tendency of organic complexants to undergo both reduction and oxidation. In the case of oxidation, however, the established influence of boric acid upon the air oxidation of organic compounds may be a contributory factor. The electrochemical reduction of complexes of boric acid and salicylic acid has been studied by polarography[284] and this technique has also shown that the complexes of boric acid with fructose[136, 571] and benzil[295] are resistant towards reduction. The reduction potential for some D-glucosazones was found to be unaffected by their complexation with boric acid, but reduction of the chelate complex was detected by polarography.[180] The resistance toward reduction shown by tungsten(VI) in some complex ions has been ascribed to electron donation by surrounding atoms, so that conversely the relative ease of reduction of tungsten in metaborotungstic acid may be related to the electronegativity of boron.[572] Other polarographic studies have shown that the 12-tungstoborate ion is more easily reduced than the phosphorus analogue[425], and the reduction of 12-borotungstic acid after neutralization and reduction has also been studied by polarography.[420]

Borax has been found to inhibit the oxidation of several sugar acids and dehydro-L-ascorbic acid in alkaline solution at ambient temperature, but it was without effect upon the oxidation of ascorbic acid.[573] An increased yield of dehydroascorbic acid obtained from the oxidation of L-ascorbic acid in the presence of borate may thus be due to stabilization of the product as a borate complex.[204] In the solid state boric acid has been found to reduce the oxidation of glucose, and complex formation may contribute to this effect.[182] Boric acid has also been found to reduce the rate of oxidation of glucose[574] and other sugars[575] in alkaline solution and since this inhibition was reduced at acid pH it is likely to be mainly a consequence of complexation. Quantitative studies of the oxidation kinetics of several borate–sugar complexes have shown that the complex itself may be oxidized[576], and the oxidation of a borate complex was detected in an examination of the effect of boric acid on the periodate oxidation of glycerol.[577] The oxidation of D-glucitol and its borate complex has also been studied[578], and complexation with boric acid has been found to retard the oxidative conversion of galactose to malonaldehyde.[579]

Thermal Stability

Many salts of complex borate anions have been subjected to thermal analysis.

Detailed information derived from these studies on the structure and composition of complexes is included under the heading of the appropriate complexant in earlier sections, and the stability results themselves are treated here. On heating the complex salts show first a loss of water of crystallization and may then dehydrate internally; the subsequent composition may be preceded by rearrangement. The stability of a given complex varies with the associated anion; in exceptional cases the compounds may persist unaltered up to 600°C[580] but usually loss of water is followed by decomposition above *ca.* 200°C. The variation in thermal stability for several metal salts of the complex of boric acid and xylitol has been studied.[581] The alkali-metal salts of the complex of boric acid with 2-methyl-2-(hydroxymethyl)-1,3,-propanediol have been reported to decompose above *ca.* 300°C with oxidation to give the appropriate alkali-metal metaborate and carbon dioxide[112], and in other work it has been reported that the sodium and potassium salts of this complex anion decompose respectively below and well above this temperature.[580] The thermal interconversion of esters of this same alcohol at lower temperatures has also been examined.[582] The thermal decomposition of a range of metal salts of borotrihydroxyglutaric acid has been studied[583] and the calcium salt of the complex of boric acid with pentaerythritol has been found to undergo loss of water up to 240°C and decomposition above this temperature.[99] The sodium salt of the 1:2 complex of boric acid with ascorbic acid has been found to be stable up to 150°C.[209] The formation and stability of complex acids of boric acid with dulcitol has been studied, and increasing temperature was reported to accomplish a conversion from the 1:1 (dulcitol:boric acid) complex acid into a 1:2 complex acid, and from the latter to a monoborate ester above 180°C.[145] The thermal properties of 12-tungstoboric acid and its ammonium salt have been studied up to 1100°C and the ammonium salt, which decomposed above 300°C, was found to be slightly more stable than the parent acid.[415] In other work sodium borotartrate was found to be stable up to 360°C and studies were also made of zinc borotartrate and the boroditartrates of lithium and magnesium.[353]

Biological Processes

Evidence for the complexation of boric acid by vitamins, enzymes and other compounds in this broad class has been summarized previously. An interaction of boric acid with biologically significant species may arise from effects other than complex formation and often reflects the presence of an established complexant as a component therein rather than the presence of this or another complexing group in the chemical structure. In other cases, particularly bacteriological processes, the borate complex may show no overall effect that has not been observed for its separate components. The bactericidal effect of sorbitol and boric acid has been studied, but could not be related to the boric acid content of the mixture.[584] It has also been observed that boric acid reduces the bacteriological action of esters of *p*-hydroxybenzoic acid.[585] The presence of borate has been reported to activate the enzyme fumarase and also alter the pH for optimum activity.[586] In the enzymic conversion of L-fucose to L-fuculose, boric acid has been found to increase the equilibrium concentration of the latter, but this may be a consequence of the interaction of boric acid with the sugar rather than the enzyme.[587] In comparisons, at the same pH, of different buffers borate has also been found to have an inhibitory effect upon the enzyme glucose-6-phosphatase.[588]

Applications

Reports of various uses which exploit the physical and chemical properties of borate complexes have appeared over a long time but do not represent a large-scale application of these compounds. Among the most significant aspects are the solvent extraction of borates as an organic complex anion and the dissolution of metals in organic solvents as gegenions to such a complex. The incorporation of borate complexes in surfactants is a new development, and their dispersant properties have also been reported to make them useful as lubricating oil components. In this application they may also act to inhibit corrosion. The gelation of boric acid with suitable complexing agents has found application in the preparation of both adhesives and drill fluids, and attempts have been made to exploit the electrical properties resulting from the formation of an ionic complex. Borate complexes have been used to catalyze the curing of resins and reflect the oxidation inhibition and fire-retardant properties established for boric acid alone. They have been reported as useful components of metal treatment baths and the biocidal, fungicidal and therapeutic properties of boron in a complex have received attention.

Depending upon the complexing agent involved, the aqueous solubility of different metals may be reduced or enhanced when they act as gegenions to a complex borate anion. Boric acid with gluconic acid has been patented as a sequestering agent to prevent the precipitation of metal ions from hard water[589, 590, 591], and in the same way sodium borogluconate has been claimed to prevent the precipitation of metal oxides after their dissolution during electrolytic derusting.[592] A mixture of boric acid or sodium perborate with a hydroxy carboxylic acid containing a terminal carboxyl group and vicinal hydroxyl groups has also been reported to be a useful sequestrant for metal ions in a washing-agent composition.[593] It has been claimed that cadmium may be precipitated from alkaline solution as a complex salt of boric acid in combination with glycerol or sorbitol[505], and a complex of boric acid with glycerol or pentaerythritol has been patented as a component of an aqueous coolant stream to prevent the dissolution of hydrogen cyanide therein.[594] Attention has also been given to the formation of complexes of boric acid with naphthalene diol as a method of removing boric acid from aqueous solution.[595]

The solubility of borate complexes in organic solvents has allowed the solvent extraction of boron from aqueous solution. Patented processes for the production of boric acid from lake brines by solvent extraction employ aliphatic polyhydric alcohols[492, 494] and aromatic alcohols related to saligenin.[489, 494] In the purification of brines containing magnesium chloride, boron removal has been effected by solvent extraction with alkyl catechols[493, 495, 596] and saligenin derivatives.[491] Alkyl-salicylic acids have also been used to extract boron from aqueous solution[487, 488], whilst in petroleum processing aqueous borax has been patented for the extraction of water-soluble hydroxy carboxylic acids from petroleum oxidation products.[597] Solvent extraction with, e.g. boric acid and glycerol, has also received attention as a means of removing basic impurities from thermally cracked naphtha.[598]

Surface-active compounds have been claimed to be formed on esterification of the reaction product of boric acid with a polyhydric alcohol, and the products were reported to contain boron in an anionic complex.[599–602] Complex formation may also be involved in the reaction of boric acid with alkylolamides, from which the products have been claimed to show surface activity.[603] A compound of boric acid with an α-hydroxy carboxylic acid has been patented for inclusion with a surface-active detergent in a washing composition[604], and reaction of boric acid with a polyhydric alcohol on heating in the presence of a carboxylic acid has been reported to give a substrate for sulphonation and application as a washing agent.[605] Amine salts of a complex of boric acid with catechol have been reported to assist the dispersion of impurities by lubricating oils.[606] An acylated polysaccharide borate has also been patented for this purpose and to increase the viscosity of a lubricating oil.[607] Complexes of boric acid with aliphatic diols have also received attention as components of petroleum fuels to reduce metal deposition after combustion of lead-containing additives therein.[608–610] A condensation product of boric acid with ethylene glycol has also been patented as a lubricating oil additive[611] and amine salts of a complex of boric acid with salicylic acid have been claimed to improve the stability and anticorrosive behaviour of lubricating oils.[612]

The reaction product of boric acid with carboxymethyl cellulose or polyvinyl alcohol has received attention as a dispersing agent in suspension polymerization[613], and other hydroxy compounds as well as cellulose have been reported to be useful as a moulding powder when compounded with boric acid.[614, 615] The gelation of aqueous vegetable gums arising from or promoted by their complexation of borate has been claimed as a method of preparing a fracture fluid for well drilling[616], and borax has been used to form gels with galacto- and gluco-mannan gums.[617] Gel formation in the presence of borax contributes to the effectiveness of starch-based adhesives[618] and borax has been used to increase and maintain the viscosity of starch and its derivatives.[619]

Borate complexes are generally highly dissociated in solution and their electrical conductivity has been recognized as having electronic applications. Electrolytes of boric acid with ethylene glycol[620] and catechol[621] have been patented for the impregnation of electrolytic capacitors, and alkylammonium salts of boric acid–catechol complexes have also been claimed for use as capacitor electrolytes.[622, 623] Other work has reported that boric acid reduces the ability of guanidine to confer insulating properties on polyethylene.[624]

A complex of boric acid with salicylic acid has been claimed to accelerate the curing of epoxy resins[625], and guanidine salts of the catechol–borate anion have been claimed as hardening catalysts[626] and curing agents[627] for 2-chloro-1,3-butadiene polymers. Complexes of boric acid with catechol have also been claimed to accelerate the vulcanization of chloroprene[628], neoprene[629] and butadiene–styrene[630] rubbers, and have received attention for the curing of butyl rubber.[631] It has also been reported that amine salts of a borate–ethylene glycol complex catalyze the reaction of fatty oils with sulphur[632], and borotungstic acid has been claimed to catalyze the conversion of cyclohexanone to its oxime by reaction with ammonia and hydrogen peroxide.[633] Boric acid complexes have also been reported to catalyze the curing of phenol–formaldehyde[634] and urea–formaldehyde[635] resins, and complex formation by boric acid with phenolic and methylol groups on a phenol–formaldehyde resin has also been claimed as a method of absorbing boric acid from aqueous solution.[636] Polymerization of isocyanates has been reported to be catalyzed by a complex of boric acid with triethylene glycol[637, 638] and boric acid–polyhydric alcohol complexes have been reported to retard foaming in the preparation of polyisocyanates.[639] The trimethyl ammonium salt of a borate–catechol complex has been claimed to catalyze the preparation of polysiloxanes[640] and boric acid–glycerol complexes have been reported to accelerate the curing of siloxane polymers.[641, 642] In other work it has been claimed that borotungstates catalyze the formation of glycol esters or their polymers.[643]

The oxidation of several polyhydric phenols has been claimed to be inhibited by a complex of boric acid with ascorbic acid[644] and a borate–saligenin complex has been claimed as an antioxidant for polypropylene.[645] The reaction products of boric acid with polyhydric alcohols and phenols[646] and with catechol and N-phenylsalicylamide[404] have been claimed as lubricating oil antioxidants and silicone fluids have been reported to be stabilized by added borate complexes.[647] Attention has been given to the stabilization of some chromium(II) compounds by combination with boric acid[444, 648] and complex formation may be involved in this effect. In other work it has been claimed that several polyhydric alcohols capable of forming boric acid complexes acted to preserve the active oxygen of sodium perborate solutions.[649] Oxidation of the complexant may however contribute to this observation. Boric acid and polyhydroxy compounds have been claimed to fireproof polyurethane foams[650] and the complexation reaction of boric acid with hydroxyl groups on a phenol–formaldehyde resin has been claimed to improve its thermal stability.[651] A complex of boric acid with glycerol or sorbitol has also received attention as part of a composition to improve the fire and heat resistance of phenolic foams.[652] Sodium borotungstate has also been claimed as a component of fire resistant paints[653] and for fabric flameproofing.[654]

The corrosion inhibition properties of 1,2-propylene glycol antifreeze and brake fluids have been improved by adding borax[655, 656], and an alkali glyceroborate has been claimed to reduce corrosion by oil-based cutting fluids.[657] The corrosion of steel by salt water has also been reported to be inhibited by an amine salt of a borate–sorbitol complex.[658] Sodium borogluconate has been claimed for use in deoxidizing baths for brass[659] and borate–polyhydric alcohol complexes have been reported to reduce scaling during the etching of aluminium.[660] Reaction products of boric acid and chromous halides have received attention as components of chromium plating baths[648] and borotungstic acid has also been claimed to improve the performance of chromium plating baths.[661] Boric acid and sodium saccharate complexes have been reported to be beneficial in nickel electroplating baths[662], and borate complexes with hydroxy carboxylic acids have also been claimed to improve the silver plating process.[663] Complexes of boric acid with tanning agents have been reported to be used for leather treatment[259] and boric acid complexes with quinone–resorcinol polymers have received attention for the same purpose.[664] Boric acid complexes with tanning compounds have also been prepared.[260, 261] Sodium sorbitol–borate has been used as a buffer in a textile finishing composition[665] and complexes of boric acid with polyhydroxy compounds have been claimed to catalyze the treatment of textile materials with resins.[666] Borotungstic acid has also been reported to be used as a component of a photosensitive system, e.g., for fabric treatment[667], and sugar–borate complexes have also been patented as paper coating materials.[668]

Amine salts of a complex of boric acid with sorbitol have been used to control microbiological growth[669] and similar salts of complex esters of boric acid 1,3-diols have received attention as bacteriocides.[670] Salts of boric acid–saligenin complexes have also been reported to have biocidal[671] and fungicidal[672] activity, and the fungicidal activity of boric acid has been reported to be increased by oxalic acid at alkaline pH.[673] The alkali-metal and ammonium salts of borotrihydroxyglutaric acid have also been claimed to have antiseptic[674] and fungicidal[675] properties, and a mixture of salicylic acid and boric acid has been patented for use as an antiseptic.[676] Sodium borotungstate has also been reported to be effective against certain virus infections[677] and calcium borogluconate has received attention as a method of increasing calcium levels in animal blood serum.[678]

Amine salts of some borate–polyhydroxy acid complexes have been claimed as therapeutic agents[679], and borate esters of some hydroxy-steroids have been reported to be effective for the treatment of arthritis.[680] A polyvinyl alcohol–boric acid–iodine complex has received attention for the treatment of eye diseases[681], and quinine and other alkaloid salts of a complex of boric acid with tartaric and salicylic acids have been claimed to reduce inflammation and infection.[682] Boric acid is known to stabilize aluminium acetate solution for therapeutic use, and a stable solid product has been obtained by evaporation of such a solution containing tartaric acid.[683] Formation of a borate complex has also been used to solubilize both dopa[684] and some polyene macrolide antibiotics[685] in water. Other patents have described the preparation of complexes of boric acid with saligenin derivatives[291, 293], dulcitol and mannitol[686, 687] and other carbohydrates.[688] In other work complex formation with boric acid has been patented as a method of separating some dihydroxy steroids[227] and vitamin B_6[215] from their associated impurities. Several enzymes have also been reported to be made insoluble in water by formation of a complex with boric acid, itself bound on a salicylic acid polymer.[219]

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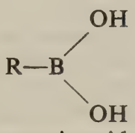
SECTION A19

BORONIC AND BORINIC ACIDS

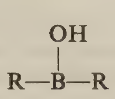
BY P. L. STRONG

INTRODUCTION

This review is concerned with the chemistry of boronic and borinic acids, which are compounds containing, respectively, two boron–oxygen bonds and one boron–carbon bond, and one boron–oxygen bond and two boron–carbon linkages. Even though borinic acids are well-known by-products in the preparation of boronic acids, they have not been investigated to anywhere near the same extent as the boronic acids. This is mainly due to the greater tendency of the borinic acids to disporportionate. The nomenclature followed has been that in commonest usage. Recent rules of the Nomenclature Committee of the American Chemical Society, however, differ considerably and are therefore noted where appropriate.[260] Boronic acids are named as alkyl or aryl dihydroxyboranes, while borinic acids are dialkyl or diaryl hydroxyboranes.



boronic acids



$$\overset{OH}{\underset{|}{}}\text{R—}\overset{|}{\text{B}}\text{—R}$$

borinic acids; R = alkyl or aryl

When used as prefixes the names are dihydroxyboryl and hydroxyborylene, respectively.

Most of the work with boronic and borinic acids as in other areas of boron chemistry has been published since 1940, when the search began for boron compounds selective for brain tumours to be used in the neutron therapy programme.[106] Since then a host of boronic-acid-containing compounds have been prepared, including pyrimidines, a variety of other heterocyclic compounds, azo dyes, diboronic acids, amino acids and many substituted aromatic derivatives.

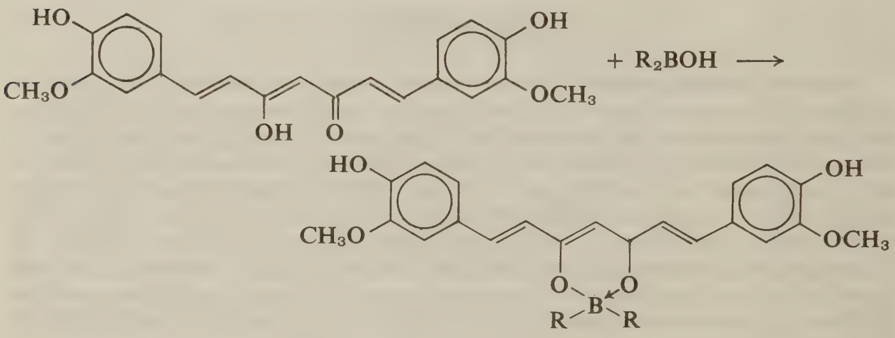
Reviews

Both boronic and borinic acids have been the subject of an excellent review containing 388 references up to 1961.[110] The outstanding work of Torrsell has been covered in a discussion[203] of reactions including nitration, sulphonation, bromination, Curtuis rearrangement, electrophilic deborination and complex formation with saccharides, and of effects on micro-organisms, enzymes and plants. Boronic and borinic acids appear in a survey of general organoboron chemistry which includes tables of physical constants.[212] The preparation, properties and reactions of boronic and borinic acids have received a general treatment.[136] The history of the development of boronic acid chemistry up to 1957 leading to a list of 59 substituted benzeneboronic acids has been given.[6] Some reference to boronic and borinic acids has been made in more general reviews of boron chemistry.[195, 197, 261–2]

Analysis

Boronic and borinic acids can be titrated as strong acids after first complexing with mannitol[96,98,208] or they can be first oxidized to boric acid by fusion with an alkali metal carbonate, nitrate or peroxide and then titrated in the presence of mannitol. Micro-determinations are usually carried out with fuming nitric acid at 440°C followed by potentiometric titration of the boric acid. Trifluoroperoxyacetic acid has been used in this application.[236–7]

Paper chromatography using *n*-butanol as solvent and alcoholic curcumin for detection gave R_f values of 0·54 for boric acid and 0·89 for *n*-butylboronic acid. Colorimetric, photometric and spectrophotometric methods for determining boronic acids involve formation of red complexes of the borinic acid with curcumin[104]:



A thin-layer chromatographic method for detection of impurities in borinic acids was developed using the procedure for formation of boroxazolidines by reaction with 1:2-aminoalcohols. These compounds are applied as ethanolic solutions to silica gel G plates and are eluted with a 3:2 mixture of chloroform–ethyl acetate.[86] In addition, boronic acids are eluted on Kieselgel G using 1 + 1 v/v chloroform–ethyl acetate as the eluting solvent. Detection is effected by spraying with a saturated ethanolic solution of turmeric, heating for 10 min at 100°C and finally spraying with 10% sodium hydroxide solution.[263]

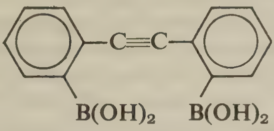
BORONIC ACIDS

Preparation of Boronic Acids

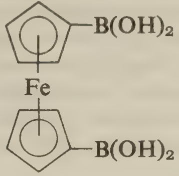
Boronic acids are most often prepared from organic esters of boric acid by reaction with a Grignard reagent followed by hydrolysis.[1,6,9,16,22,26,37,46,65,74,89,125,127,129,132,140,190,209,211–12]

$$RMgX + B(OR)_3 \rightarrow RB(OR)_2 \xrightarrow{H_2O} RB(OH)_2$$

Use of tetrahydrofuran as solvent in place of ether has given slightly better yields.[34] Both alkyl and aryl diboronic acids[211] and alkene boronic acids[67,106,259] have been prepared in this manner. Mechanism studies of the Grignard reaction with alkyl borates have shown the formation of the complex, $RB(OR)_3MgBr$, to be involved.[34] Boron trihalides may be used instead of esters.[6] Organolithium derivatives are often needed in place of the magnesium Grignard reagent; this appears to be especially true for more complex syntheses such as the preparation of hydroxy and amino boronic acids.[6] Pyridine[24], picoline[24], thiophene[150], and ferrocenyl boronic acids[134, 163, 226, 239] as well as 2:2′-tolandiboronic acid[190] and ferrocenediboronic acid[177] were all prepared using the lithium reagent. For example:

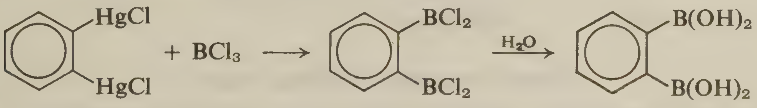


2,2′-tolandiboronic acid



ferrocenediboronic acid

In addition, organomercury derivatives are used, usually with boron halides rather than with esters.[6, 154] Examples are the preparation of 1:2-benzenediboronic acid[143] and iodomethaneboronic acid[169, 248]:



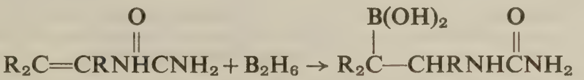
$$ICH_2HgI + BBr_3 \xrightarrow{NaI} ICH_2BBr_2 \xrightarrow[(2)\ H_2O]{(1)\ n\text{-}C_4H_7OH} ICH_2B(OH)_2$$

The reaction of biphenylene with boron tribromide and aluminium chloride or bromide gave, after hydrolysis, biphenylene-2-boronic acid and a diboronic acid presumed to be the 2:6-derivative. Powdered aluminium has been used as a catalyst in this type of reaction.[253] Composition of the product could be changed by varying the ratio of aluminium dust to boron tribromide.

Oxidation of trialkylboranes to the corresponding alkylboronic acids is usually carried out with oxygen, hydrogen peroxide or perbenzoic acid.[1, 25, 212] The use of *N*-oxides in this reaction is claimed to give cleaner products and better yields[186]:

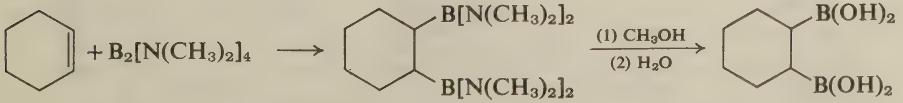
$$R_3B + 2R_3N \rightarrow O \xrightarrow{H_2O} RB(OH)_2 + 2R_3N + 2ROH$$

Boronic acids and many diboronic acids, both 1:1- and 1:2-substituted, have been prepared by hydroboration of unsaturated materials with diborane.[47–8, 116, 121, 181, 198] This method was utilized to prepare boronic-acid-substituted ureas and carbamates[111, 142] in the typical two-stage reaction involving hydrolysis in the second step:



$$R_2C{=}CRNH\overset{\overset{\displaystyle O}{\|}}{C}NH_2 + B_2H_6 \rightarrow R_2\overset{\overset{\displaystyle B(OH)_2}{|}}{C}{-}CHRNH\overset{\overset{\displaystyle O}{\|}}{C}NH_2$$

The fact that only one boronic acid was formed rather than mixtures was attributed to co-ordination of the diborane with the amino nitrogen, thus forming a 6-membered ring. A related reaction is the preparation of 1:2-*cyclo*hexane diboronic acid and 1:2-ethanediboronic acid by addition of tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, to *cyclo*hexene, followed by hydrolysis[91]:



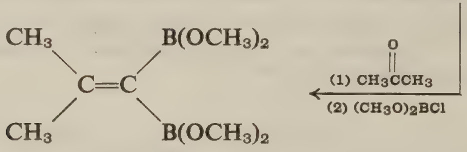
Boronic acids are often prepared from other boron derivatives by hydrolysis, as shown in the above equation. Examples are boron halides[43] and borazoles.[39] An unusual boron derivative is obtained by the isolation of hydromethylboronic acid from the hydrolysis of borane(3)carbonyl, BH_3,CO[156]:

$$H_3B,CO + H_2O \rightarrow (HO)_2BCH_2OH$$

An interesting new approach for the preparation of aromatic boronic acids involves dihalogenoboryl radicals formed by irradiation of boron trihalides in the presence of aromatic compounds. Yields are usually low, however, and more work needs to be done to optimize the conditions and to determine the reaction mechanism.[75, 151, 210]

A novel approach to the synthesis of alkeneboronic acids was utilized in the preparation of 2-methylpropene-1:1-diboronate. This method involves the recently reported octamethyl methanetetraboronate[196] which reacts with methyllithium to give the trimethoxyboryl carbanion as a readily transferable nucleophilic unit. This carbanion reacts with ketones or aldehydes or give alkene-1:1-diboronic acids[225, 271]:

$$[(CH_3O)_2B]_4C + CH_3Li \rightarrow [(CH_3O)_2B]_3C]^- Li^+$$



Physical Properties of Boronic Acids

Boronic acids are usually crystalline solids which give the characteristic green flame displayed by most boron compounds. Alkylboronic acids are readily soluble in organic solvents and water. They are volatile in air and steam, and have a terpene-like odour and a sweet taste.[25] Arylboronic acids are soluble in hot water and polar solvents. Their salts are white crystalline materials, soluble in hydroxylic solvents and insoluble in non-polar media; decomposition points are reported since they do not melt.[100] Melting points of the free boronic acids are often difficult to reproduce owing to ready dehydration to the anhydrides, which themselves have more characteristic melting points. However, melting points of most boronic acids are reported and are included in Table I. This Table is primarily intended to indicate the large variety of boronic acids, both simple and complex, which has been reported. It is not all-inclusive, since representative examples are included and many compounds of each type are omitted; however, the cited references contain information on compounds of similar type.

Table I.—Boronic Acids: Formulæ, Melting Points and References

Alkyl and Unsubstituted Aromatic Boronic Acids

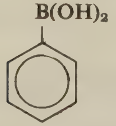
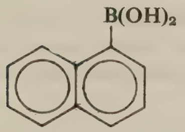
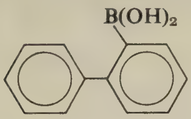
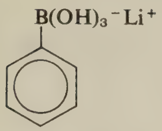
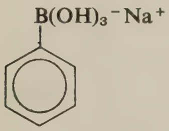
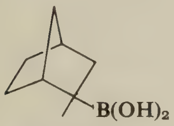
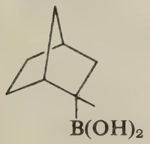
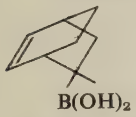
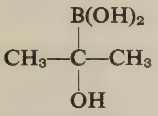
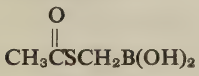
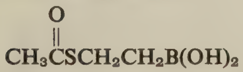
Formula	Melting point (°C)	References
1. $CH_3B(OH)_2$	95–100° (sublimes 100°)	1
2. $CH_3CH_2CH_2B(OH)_2$	105–110°	1
	107°	10
3. $CH_3CH_2CH_2CH_2B(OH)_2$	93–94°	1
	85–87°	3
4. $CH_3CH_2CH(CH_3)B(OH)_2$	112°	1
5. $(CH_3)_3CB(OH)_2$	113°	1
6. 	218–220°	86
	220–221°	1, 208
	210–213°	141
	215–216°	259
7. 	225–227°	74

Table I.—(continued)

Alkyl and Unsubstituted Aromatic Boronic Acids

Formula	Melting point (°C)	References
8. 	290°(decomp.)	200
9. 	115°(decomp.)	100
10. 	170°(decomp.)	100
11. 	—	137
12. 	105°(decomp.)	137
13. 	86–90°	189
14. $HOCH_2B(OH)_2$	—	154
15.  $CH_3\text{—}\underset{OH}{\overset{B(OH)_2}{C}}\text{—}CH_3$	151–153°(decomp.)	148
16. $ICH_2B(OH)_2$	70–71°	169
17.  $CH_3\overset{O}{\overset{\|}{C}}SCH_2B(OH)_2$	100–101°	169
18.  $CH_3\overset{O}{\overset{\|}{C}}SCH_2CH_2B(OH)_2$	72–75°	147
19. $HO_2CCH_2SCH_2CH_2B(OH)_2$	104–108°	147

Di- and tetra-boronic acids

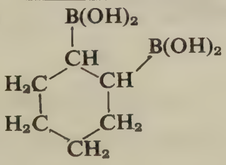
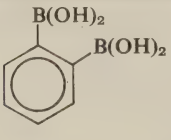
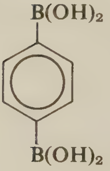
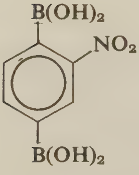
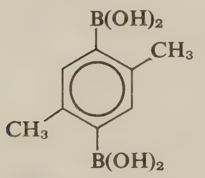
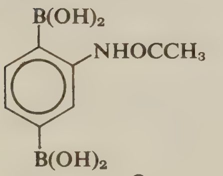
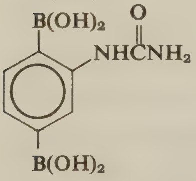
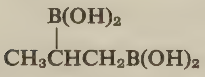
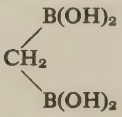
Formula	Melting point (°C)	References
20. 	—	91

Table I.—(continued)

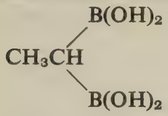
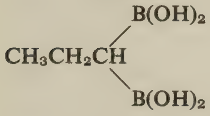
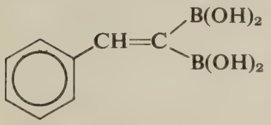
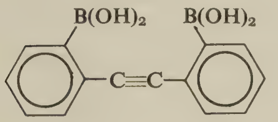
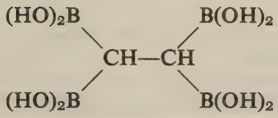
Di- and tetra-boronic acids

Formula	Melting point (°C)	References
21. 	104–105°(decomp.)	143
22. 	> 350°	194
23. 	> 350°	194
24. 	> 350°	85
25. 	> 350°, having formed the monoanhydride	194
26. 	> 350°, having formed the monoanhydride	194
27. $(HO)_2BCH_2CH_2B(OH)_2$	195–198° 180–190°(decomp.) 100–120°	84 116 197
28.  $CH_3\overset{\overset{B(OH)_2}{\vert}}{C}HCH_2B(OH)_2$	160°(decomp.)—slow heating 170–177°(decomp.) immersed at 140° and heated rapidly	181
29. $(HO)_2B(CH_2)_4B(OH)_2$	179–181°	43
30.  $CH_2(B(OH)_2)_2$	155–155·5°	154

Refs. p. 806

Table I.—(continued)

Di- and tetra-boronic acids

Formula	Melting point (°C)	References
31.  $CH_3CH(B(OH)_2)_2$	148–150° 142–150°(decomp.)	198 116
32.  $CH_3CH_2CH(B(OH)_2)_2$	133–136°(decomp.)	181
33. 	110°(decomp.)	225
34. 	233–234°	190
35. 	decomp.	82

Vinyl boronic acids

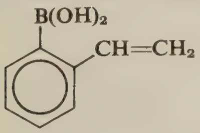
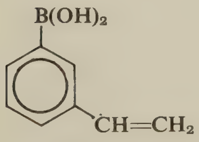
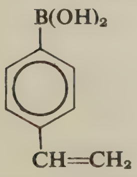
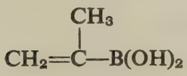
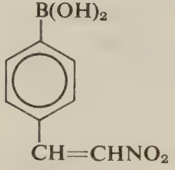
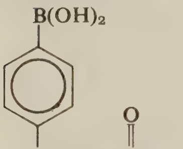
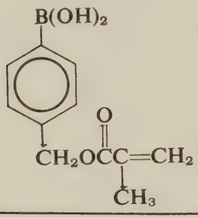
Formula	Melting point (°C)	References
36. 	100–109° 110–112°	65
37. 	145–160° 143–145°	65 259
38. 	188–189° 190–191°	65 259
39. $CH_2{=}CHB(OH)_2$	74°	125
40. $CH_3CH{=}CHB(OH)_2$	82–85° 86–87°	106 125
41.  $CH_2{=}C(CH_3){-}B(OH)_2$	78–80°	125
42. $(CH_3)_2C{=}CHB(OH)_2$	87°	125

Table I.—(continued)

Vinyl boronic acids

Formula	Melting point (°C)	References
43. 	289–290°(decomp.)	191
44. 	205–212°	191
45. 	119·5–121°	172

Substituted aromatic boronic acids

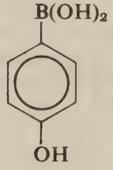
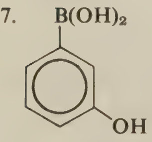
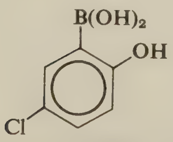
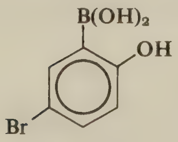
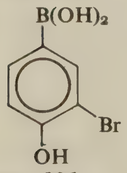
Formula	Melting point (°C)	References
46. 	240°(decomp.)	92
47. 	225°(decomp.)	209
48. 	241–242°	77
49. 	187·5–190° 190°	3 254
50. 	191–192°	57

Table I.—(continued)

Substituted aromatic boronic acids

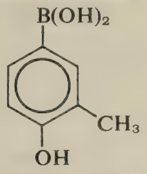
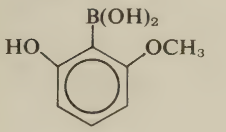
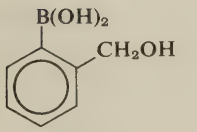
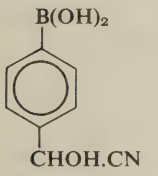
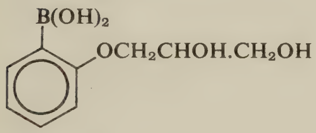
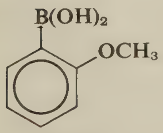
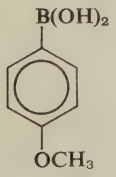
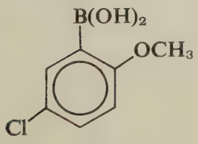
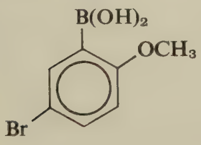
Formula	Melting point (°C)	References
51. 	266–268°(decomp.)	209
52. 	100–101°	3
53. 	97–98°	202
54. 	approx. 104°	191
55. 	133–135°(2 torr) 177–180°(19 torr)	57 69
56. 	106–109°	259
57. 	208–210°	259
58. 	144–145°	77
59. 	130·5–131°	3

Table I.—(continued)

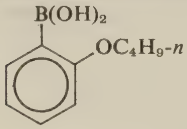
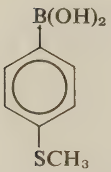
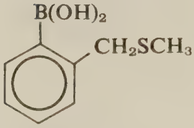
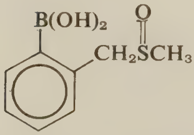
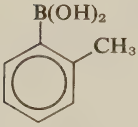
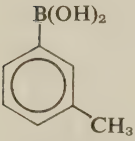
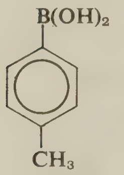
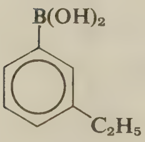
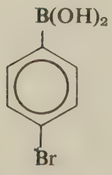
Substituted aromatic boronic acids		
Formula	Melting point (°C)	References
60. 	209–210°	83
61. 	209–209·5°	3, 254
62. 	approx. 58°	149, 160
63. 	104·5°	149, 160
64. 	166–168°	259
65. 	166–167°	259
66. 	261–262·5°	259
67. 	93–93·5°	259
68. 	286–289°	209

Table I.—(continued)

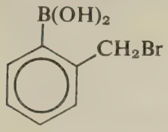
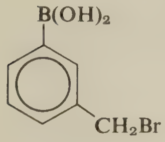
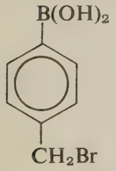
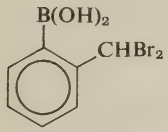
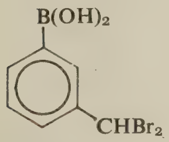
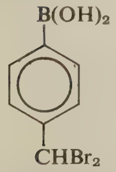
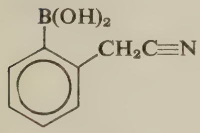
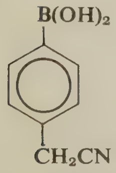
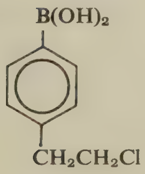
Substituted aromatic boronic acids		
Formula	Melting point (°C)	References
69. 	142–148° 139–146° 143–150°	202 191 160
70. 	214–216°	202
71. 	165–168° 138–144°	202 191
72. 	163°	202
73. 	160–165°	202
74. 	160–170°(decomp.)	202
75. 	85°, dehydrates, melts 150–152°	155, 180
76. 	214–215°	57
77. 	188–193°	57

Table I.—(continued)

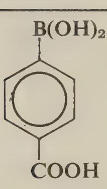
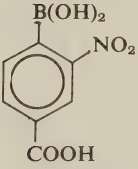
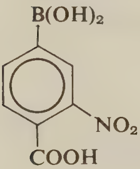
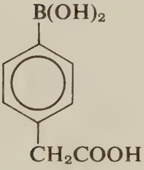
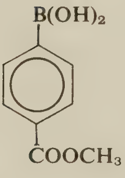
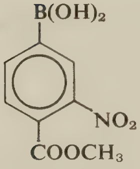
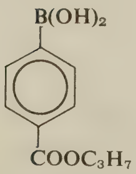
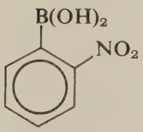
Substituted aromatic boronic acids		
Formula	Melting point (°C)	References
78. 	219–220° —	191 92
79. 	250–260°(decomp.)	14, 19
80. 	220–230°(decomp.)	204
81. 	165–166°	57
82. 	230–233°	209
83. 	242–244°	204
84. 	162–164°	57
85. 	139·2–140·8° 140–142°	208 153

Table I.—(continued)

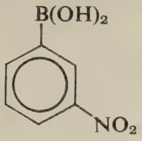
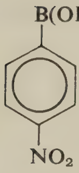
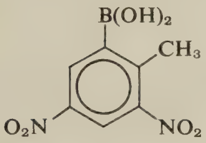
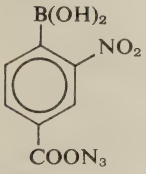
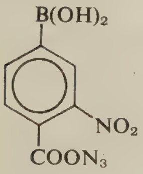
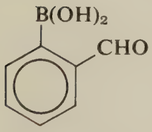
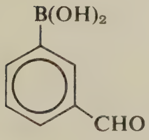
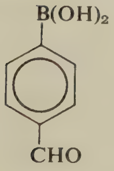
Substituted aromatic boronic acids		
Formula	Melting point (°C)	References
86. 	273°	36
87. 	305°(decomp.)	208
88. 	142°	14
89. 	110°(decomp.)	209
90. 	oil	204
91. 	115–123° 118–120° 120–123° 110–120°	202 191 192, 259 166
92. 	112°	202
93. 	230–240°, sinters to glassy mass, 240°	202 191

Table I.—(continued)

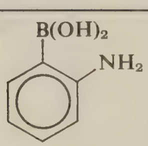
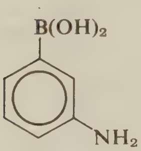
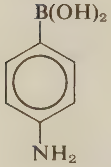
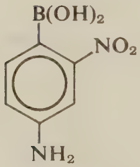
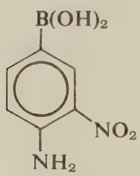
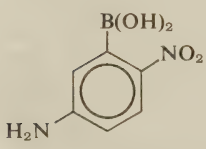
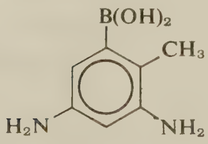
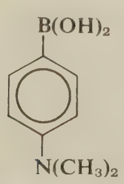
Amino-boronic acids and their derivatives		
Formula	Melting point (°C)	References
94. 	179–180° 175–176°	209 153
95. 	92·8–93·8°	208
96. 	> 300°	92
97. 	142–143°(decomp.)	209
98. 	224°(decomp.)	204
99. 	250–255°(decomp.)	14
100. 	163°(decomp.)	14
101. $H_2NCH_2CH_2B(OH)_2.2H_2O$	160°(decomp.)	165
102. 	270–275° 125°	14

Table I.—(continued)

Amino-boronic acids and their derivatives

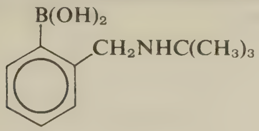
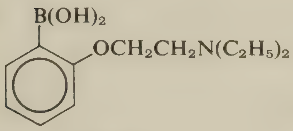
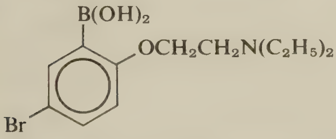
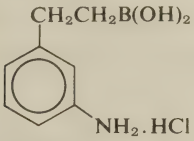
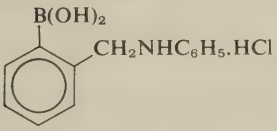
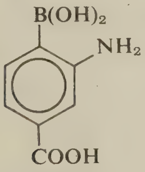
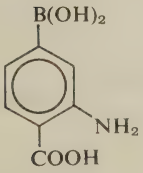
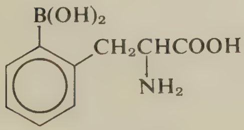
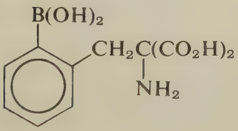
Formula	Melting point (°C)	References
103. 	135–137°	146
104. 	116–118° 115–118°	57 69
105. 	164–167°	168
106. $(C_3H_7)_2NCH_2CH_2CH_2B(OH)_2$	107°	99
107. 	190–192°	187
108. 	169–171°(decomp.)	146
109. $[H_3N^+CH_2CH_2B(OH)_2]^+Br^-$	106–108°	165
110. 	180–190°(decomp.)	209
111. 	> 360°	204
112. 	252–262° having formed its anhydride	164, 174
113. 	—	54

Table I.—(continued)

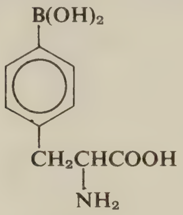
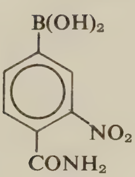
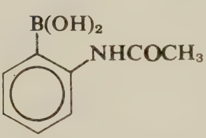
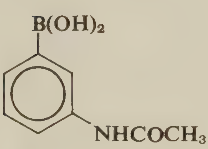
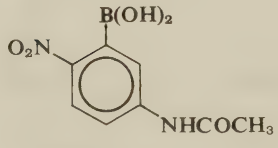
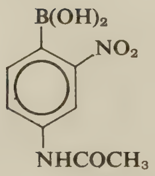
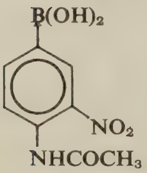
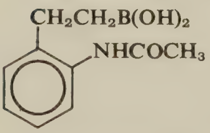
Amino-boronic acids and their derivatives		
Formula	**Melting point (°C)**	**References**
114. 	285–290°(decomp.)	191
115. 	252°(decomp.)	204
116. 	300–301°	194
117. 	250° 274–275°	14 204
118. 	193–196°	14
119. 	230–231°	209
120. 	246°(decomp.)	204
121. 	> 127°	187
122. $CH_3CONHCH_2CH_2B(OH)_2$	90–95°	165

Table I.—(continued)

Amino-boronic acids and their derivatives

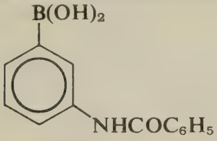
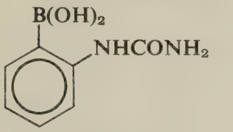
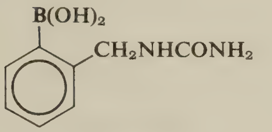
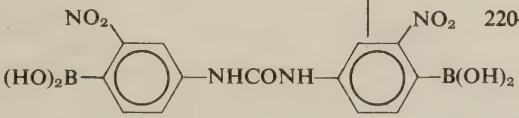
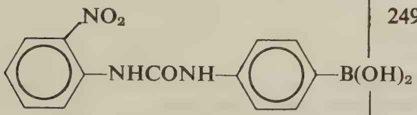
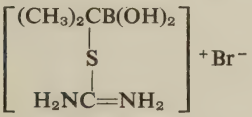
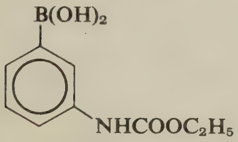
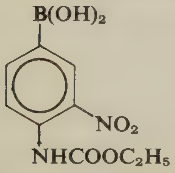
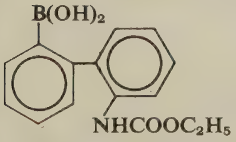
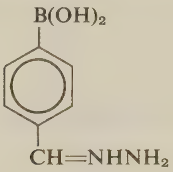
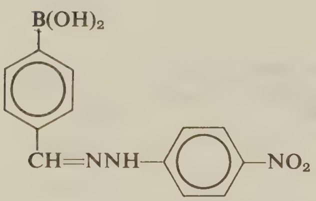
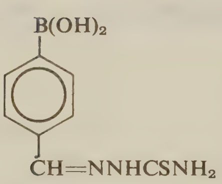
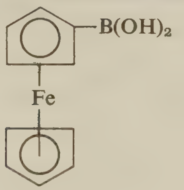
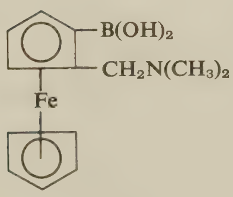
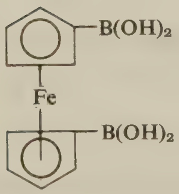
Formula	Melting point (°C)	References
123. 	290°(decomp.)	209
124. 	Indefinite	142
125. 	215–218° on fast heating 200–203° changes to needles, melts 240°	54
126. 	220–230°(decomp.)	209
127. 	249°(decomp.)	204
128. $H_2NCONHCH_2CH_2B(OH)_2$	102–104°	111, 142
129. $CH_3CONHCONHCH_2CH_2B(OH)_2$	227–228°	165
130.  $\left[\begin{array}{c}(CH_3)_2CB(OH)_2\\ S\\ H_2NC{=}NH_2\end{array}\right]^{+}Br^{-}$	130–200°(decomp.)	148
131. 	202–203°	14
132. 	209°	204
133. 	215–220°, having formed its anhydride	124
134. $C_6H_5CH_2OCONHCH_2CH_2B(OH)_2$	106–108°	142

Table I.—(continued)

Amino-boronic acids and their derivatives

Formula	Melting point (°C)	References
135. $C_2H_5OCONHCH_2CH_2B(OH)_2$	71–73°	142
136. 	295°	191
137. 	280°	202
138. 	204–205°	202

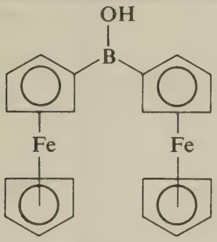
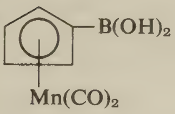
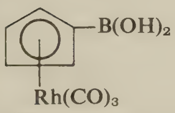
Boronic and borinic acid transition metal complexes

Formula	Melting point (°C)	References
139. 	143–148°(decomp.) 142–148°	239 177
140. 	177–178°	134, 163, 171
141. 	180°(decomp.)	177

Refs. p. 806

Table I.—(continued)

Boronic and borinic acid transition metal complexes

Formula	Melting point (°C)	References
142. 	159–161°	239
143. 	204–214°	226
144. 	221°(decomp.)	226

Heterocyclic boronic and borinic acids

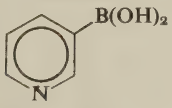
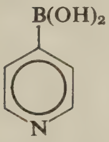
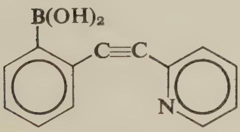
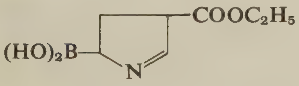
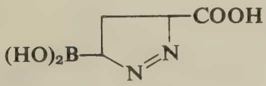
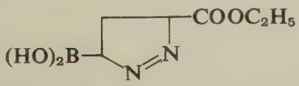
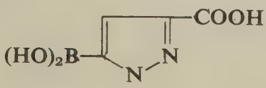
Formula	Melting point (°C)	References
145. 	>300°	94, 108
146. 	>300°	108
147. 	135°	56, 73
148. 	196–198°	147
149. 	196·5–197·5°	138
150. 	195–210°	138
151. 	196·5–197·5°(decomp.)	38

Table I.—(continued)

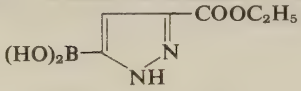
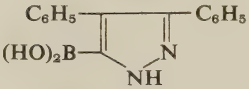
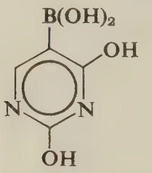
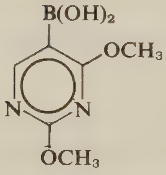
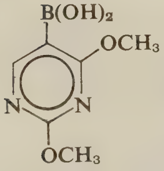
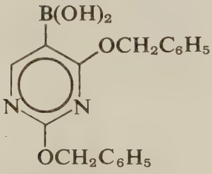
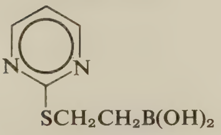
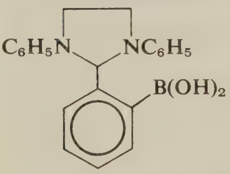
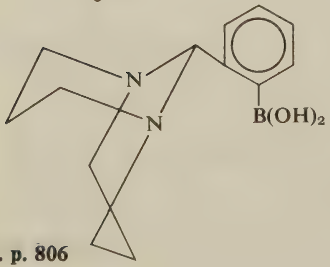
Heterocyclic boronic and borinic acids		
Formula	Melting point (°C)	References
152. 	196–198°	38
153. 	170–174°	38
154. 	approx. 330°(decomp.)	90
155. 	115–117°	152
156.  $\cdot 5H_2O$	115–117°	90
157. 	87–89°	152
158. 	108–111°	147
159. 	144–146°	166
160. 	297–299°	166

Table I.—(continued)

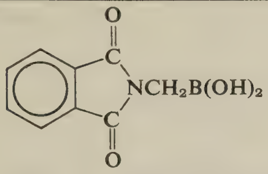
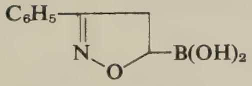
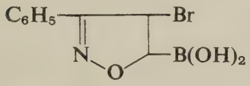
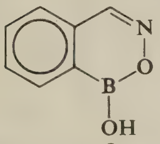
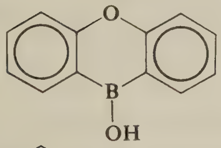
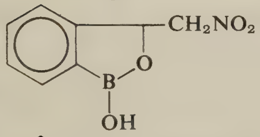
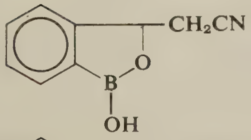
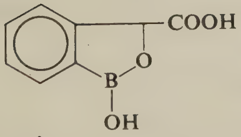
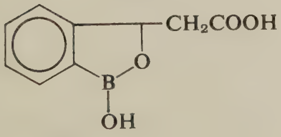
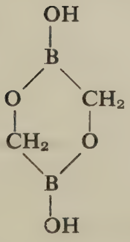
Heterocyclic boronic and borinic acids		
Formula	Melting point (°C)	References
161. 	134–135°	169
162. 	123–124°	159
163. 	116°	159
164. 	264–265°	192
165. 	258–263°	253
166. 	117–119°	166
167. 	107–109°	166
168. 	141–142°	166
169. 	128–130°	178
170. 	147–148°	154, 156, 169, 247

Table I.—(continued)

Heterocyclic boronic and borinic acids

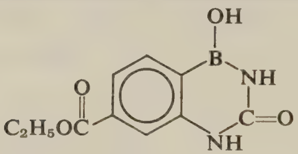
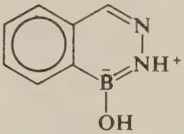
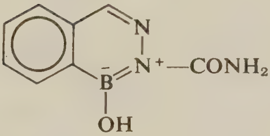
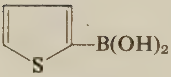
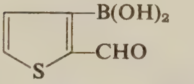
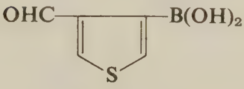
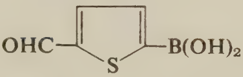
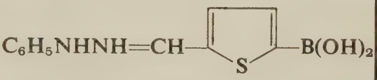
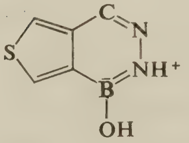
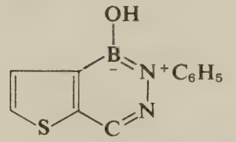
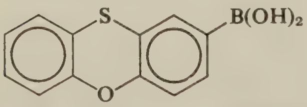
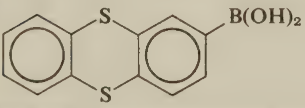
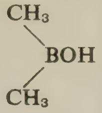
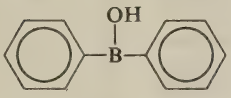
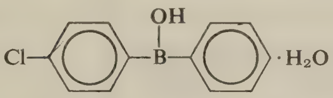
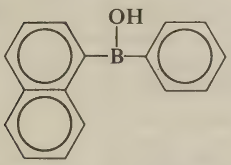
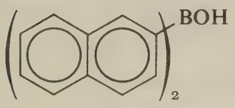
Formula	Melting point (°C)	References
171. 	> 350°	165
172. 	243–243·5°, having formed its anhydride	192
173. 	295–299°	166
174. 	123–125°	86
175. 	(decomp.)	150
176. 	135–180°(decomp.)	150
177. 	(decomp.)	150
178. 	130–140°(decomp.)	150
179. 	150–164°(decomp.)	150
180. 	147–153°	150
181. 	156·8–157·5°	3, 254
182. 	dehydrates 170°, melts 215–216° 210	254 3

Table II.—Borinic Acids: Formulæ, Melting Points and References

Formula	Melting point (°C)	References
183.  $\begin{array}{l} CH_3 \\ \quad \diagdown \\ \quad\; BOH \\ \quad \diagup \\ CH_3 \end{array}$	b.p. 56° (760 mm)	175
184. 	264°	1
185. 	Unstable oil	16
186. 	oil	161
187. 	105–106°	161

Cryoscopic molecular-weight experiments indicate no dimerization or association for aryl- or alkylboronic acids in nitrobenzene or dioxane. However, some association was indicated in benzene. Dipole-moment data indicate no association in either benzene or dioxane.[1, 212]

The strong infra-red absorption of boron–oxygen in the 1,300–1,400 cm^{-1} region when accompanied by an absorption in the 3,200–3,450 cm^{-1} (hydroxyl region) is a valuable aid in recognizing the BOH functional group.[9, 11, 12, 172, 178] Diboronic acids show two absorptions in the hydroxyl region, one at lower frequency attributed to hydrogen bonding and one without hydrogen bonding. Monoboronic acids show only the hydrogen-bonding absorption.[211] Salts of boronic acids usually absorb at a lower wave number.[6, 18] In addition, a band at 1,020–1,030 cm^{-1} is assigned to the boronic acid function.[254] Disappearance of this band and the hydroxyl absorption in the 3,300 cm^{-1} region, when accompanied by a strong absorption between 680–704 cm^{-1}, are indicative of formation of the boronic anhydride.[129, 254, 268]

A review of ultra-violet studies of boronic acids has been reported.[206] In order to obtain reproducible spectra, the free acids should be examined in aqueous solvents to avoid dehydration to the anhydride. Conversely, ultra-violet spectra of boronic anhydrides should be carried out in anhydrous systems.

Benzeneboronic acid gives an ultra-violet spectrum similar to that of a substituted benzene and essentially the same as that of a benzoate anion. Substituent effects are smaller for the boronic acid, however.[206]

Ultra-violet evidence for electron delocalization between the phenyl group and boron has been obtained.[206, 163, 259] Also, delocalization from oxygen to boron was supported and this delocalization is said to be greater with boron–oxygen than with boron–halogen groups. Methyl groups on aromatic rings have very little influence. The electronic structures and spectra of benzene, toluene and styryl boronic acids were calculated using the Pariser–Parr–Pople method.[158]

^{11}B-nuclear-magnetic-resonance (n.m.r.) chemical shifts for methyl-, butyl- and

Table III.—*Ultra-violet Spectra of Boronic Acids and Anhydrides: Absorption Maxima, λ_1–λ_3, and Molar Absorptivities, ϵ_1–ϵ_3*

Structure	Solvent	λ_1	ϵ_1	λ_2	ϵ_2	λ_3	ϵ_3	Reference
1. $C_6H_5B(OH)_2$	Water	190	50,000	218	8,600	266	452	206
2. $C_5H_5B(OH)_2$	95% ethanol			219	11,000	267	480	252
3. $(C_6H_5BO)_3$	*n*-hexane, *cyclo*hexane	193	113,000	236	75,500	273	2,500	206
4. C_6H_6	95% ethanol			203	8,000	253	230	252
5. *p*-$BrC_6H_4B(OH)_2$	Water	196	35,000	231·5	14,500	266	400	206
6. (*p*-$BrC_6H_4BO)_3$	*n*-hexane, *cyclo*hexane, heptane	205	81,000	253·3	86,500	277	2,000	206
7. *o*-$CH_3C_6H_4B(OH)_2$	95% ethanol			210	8,300	270	530	252
8. *p*-$CH_3C_6H_4B(OH)_2$	95% ethanol			206	7,900	263	390	252
9. $CH_3C_6H_5$	95% ethanol			206	7,200	263	270	252
10. *o*-$CH_3OC_6H_4B(OH)_2$	95% ethanol			225	8,200	280	2,600	252
11. *p*-$CH_3OC_6H_4B(OH)_2$	95% ethanol			236	12,500	272	1,200	252
12. $CH_3OC_6H_5$	95% ethanol			218	8,000	271	1,900	252
13. *p*-$HOOCC_6H_4B(OH)_2$	95% ethanol			232	14,000	380	1,050	252
14. C_6H_5COOH	95% ethanol			225	9,800	272	860	252
15. $C_6H_{11}B(OH)_2$	95% ethanol			204	20	—	—	252
16. $C_6H_{11}B(OH)_2$	98+2 *cyclo*hexane–methanol			216	15			252
17. $B(OH)_3$	98+2 *cyclo*hexane–methanol			227	25			252
18. 2-C_6H_5–C_6H_4–$B(OH)_2$	95% ethanol	247	43,600	343	2,900	360	5,760	199
			(also	254	70,800	346	3,900)	
19. 2:6- or 2:7-$[(HO)_2B]$–C_6H_3–C_6H_5	95% ethanol	254	61,600	364	6,030	260	81,000	199
			(also	366	4,570)			

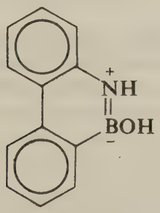
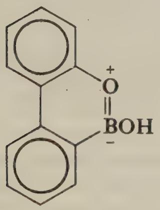
Table IV.—^{11}B-n.m.r. Data for some Boronic Acids with Trimethylborate as Reference[193]

Compound	Chemical shift, δ
$B(OH)_3$	−0·7
$CH_3B(OH)_2 \cdot H_2O$	−13·8
$(CH_3BO)_3$	−15·1
$(CH_3)_2BOH$	−36·5
$C_4H_9B(OH)_2$	−14·3
$C_6H_5B(OH)_2$	−15·2

benzeneboronic acid have been recorded along with data for the anhydride and borinic acid of the methyl derivative (Table IV).

^{11}B-n.m.r. spectroscopy has been an important tool in investigating the mechanism of salt formation between the boronic acids and a base. The usual pathway involves addition of the base to the boron atom and this leads to a large upfield shift ($\sim$25 p.p.m.) accompanied by a narrowing of the ^{11}B resonance. Salt formation with loss of a proton leads to a downfield shift (approx. 5 p.p.m.) and a large broadening of the ^{11}B resonance. These data are illustrated in Table V.

Table V.—Effect of Salt Formation on ^{11}B Resonance in Boronic Acids[133]

Compound	Solvent	Chemical shift (p.p.m. relative to boron trifluoride etherate)	Line width (Hz)
	Ethanol Ethanol–5% KOH	−29·3 −43·9	221 2,500
	Ethanol Ethanol–5% KOH	−28·8 −5·5	233 162
$C_6H_5B(OH)_2$	Ethanol Ethanol–5% KOH	−28·4 −3·2	272 80

Proton n.m.r. data are recorded in Table VI. It should be kept in mind that OH resonances are sensitive to temperature and concentration owing to hydrogen-bonding effects.

The calculated p.m.r. and ^{11}B-n.m.r. spectra of a series of *p*-substituted benzene–boronic acids revealed a linear correlation with Hammett σ constants indicating the possibility for n.m.r. use in determining substituent effects on electron densities.[92]

A mass-spectral study of ferrocenylboronic acid showed no rearrangements which might involve Fe–O bond formation. Intramolecular hydrogen bonding involving

Table VI.—P.M.R. Data for Boronic acids, Relative to Tetramethyl Silane at Room Temperature

Compound	Solvent	τ(OH)	J(^{13}CH)	τ(CH_3)	Reference
$B(OH)_3$	D_2O	4·54			193
$CH_3B(OH)_2$	D_2O	5·02	116	9·54	193
$(CH_3)_2B(OH)$	Neat liquid	6·65	117	9·97	193
$(CH_3BO)_3$	Neat liquid		117	9·73	193
2-C_6H_5-C_6H_4-$B(OH)_2$	$(CH_3)_2SO$	2·4			199
$ICH_2B(OH)_2$	D_2O	5·43		(CH_2) 7·75	169

the BOH group and Fe atom was also not observed. The mass spectrum of ferrocenylboronic acid was compared with that of phenylboronic acid and the two aromatic boronic acids were shown to display very different patterns. Hydroxyl radical loss was important in the phenyl analogue while elimination of water was more important for the ferrocene compound. Evidence favoured a weaker bond for phenyl–boron than for ferrocene–boron.[239, 269]

An electron-diffraction study of methaneboronic anhydride indicates that the methyl groups are bonded to boron and are in the plane of the boroxine ring.[255]

The heat of hydrolysis of liquid *n*-butylboronic anhydride in giving solid *n*-butylboronic acid was determined as −48·5 ± 0·6 kJ mole^{-1} (−11·6 ± 0·15 kcal mole^{-1}). The heat of solution of *n*-butylboronic acid in water is 11·2 ± 0·3 kJ mole^{-1} (2·67 ± 0·06 kcal mole^{-1}).[201] For methane–boronic acid the heat of sublimation was found to be 64·0 kJ mole^{-1} (15·3 kcal mole^{-1}).

Chemical Properties of Boronic Acids

GENERAL REACTIVITY

Boronic acids are comparable to aldehydes in that they reduce Fehling's solution and on dehydration they yield trimers which are similar to those obtained from aldehydes.[6] Boronic acids are electron-deficient molecules and as such they possess a high degree of electrophilic reactivity. This behaviour is evidenced by the formation of co-ordination compounds and by their rather special behaviour with bases. Aqueous solutions of boronic acids are weakly acidic[1, 187]; however, they can be titrated as strong acids after co-ordination with mannitol.[15] This increase in acidity on co-ordination with polyhydroxy compounds is general and emphasizes the fact that boronic acids are not proton donors but are hydroxide acceptors.[52, 129] The variation of dissociation constants of aromatic boronic acids with methanol concentration in aqueous methanol differs from that of other organic acids.[157] Acid-dissociation constants have been measured for many acids. Phenylboronic acid is three times as strong as boric acid. Alkyl-substituted boronic acids are about one-tenth as strong as the phenyl derivatives[136], and benzylboronic acid has about the same strength as phenylboronic acid. The acidity of boronic acids is increased by substitution of electronegative groups and decreased by *ortho* substitution.[212] Dissociation constants of several boronic acids are listed in Table VII. As mentioned above, boronic acids are readily converted to anhydrides and salts.[212]

Aqueous solutions of boronic acids reduce hot alcoholic silver nitrate solution.[25] They are more stable towards air oxidation than the corresponding borinic acids and boranes and in this context, aromatic boronic acids are more stable than their aliphatic counterparts.[9, 48, 212] Polymethylenediboronic acids are more resistant to oxidation than the monoboronic acid derivatives. Aromatic diboronic acids require temperatures greater than 230°C for dehydration and the resulting anhydride polymers melt at above 400°C. Mono-aminobenzeneboronic acids decompose on exposure to air; the acetyl derivatives are, however, stable. Also, toluene–boronic acids decompose during nitration while carboxy and nitro derivatives do not.[14]

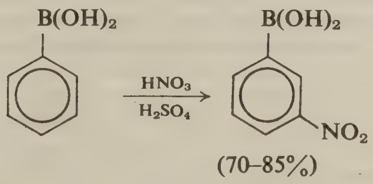
Optically active 1-phenylethylboronic acid is readily auto-oxidized, especially in

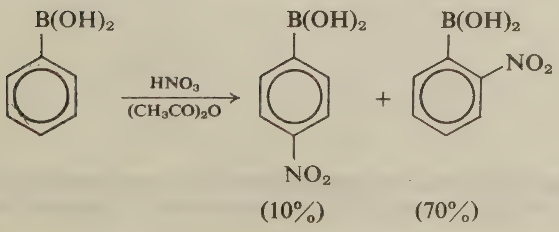
Table VII.—Dissociation Constants of Boronic Acids

Compound	K_a ($\times 10^{-10}$)	Solvent	Reference
Phenylboronic acid	13·7 (19)	H_2O	219 (35)
	1·97	25% aq. C_2H_5OH	219, 218, 222
	1·64	50% aq. C_2H_5OH	219, 218
o-Tolylboronic acid	1·81	H_2O	219
	0·261	25% aq. C_2H_5OH	219
m-Tolylboronic acid	1·40	25% aq. C_2H_5OH	219
p-Tolylboronic acid	1·00	25% aq. C_2H_5OH	219
o-Chlorophenylboronic acid	14·0	25% aq. C_2H_5OH	217
m-Chlorophenylboronic acid	14·5 (13·5)	25% aq. C_2H_5OH	217 (218)
p-Chlorophenylboronic acid	6·23 (6·30)	25% aq. C_2H_5OH	217 (218)
m-Fluorophenylboronic acid	11·0	25% aq. C_2H_5OH	218
p-Fluorophenylboronic acid	3·66	25% aq. C_2H_5OH	218
m-Bromophenylboronic acid	14·6	25% aq. C_2H_5OH	218
p-Bromophenylboronic acid	7·26	25% aq. C_2H_5OH	218
o-Nitrophenylboronic acid	5·6	25% aq. C_2H_5OH	218
m-Nitrophenylboronic acid	69	25% aq. C_2H_5OH	218
p-Nitrophenylboronic acid	98	25% aq. C_2H_5OH	218
m-Carboxyphenylboronic acid	1·12 (2nd K_a)	25% aq. C_2H_5OH	218
p-Carboxyphenylboronic acid	1·90 (2nd K_a)	25% aq. C_2H_5OH	218
p-Phenoxyphenylboronic acid	0·116	50% aq. C_2H_5OH	218
o-Phenethylboronic acid	0·910	25% aq. C_2H_5OH	217
m-Phenethylboronic acid	3·05	25% aq. C_2H_5OH	217
p-Phenethylboronic acid	0·608	25% aq. C_2H_5OH	217
	0·116	50% aq. C_2H_5OH	218
α-Naphthylboronic acid	0·888	25% aq. C_2H_5OH	219
β-Naphthylboronic acid	2·60	25% aq. C_2H_5OH	219
Benzylboronic acid	7·55	H_2O	219
	1·49	25% aq. C_2H_5OH	219
β-Phenethylboronic acid	1·00	H_2O	219
	0·181	25% aq. C_2H_5OH	219
n-Butylboronic acid	0·182	H_2O	219
	0·0344	25% aq. C_2H_5OH	219
o-Diphenylylboronic acid	0·00984	50% aq. C_2H_5OH	219
m-Diphenylylboronic acid	0·185	50% aq. C_2H_5OH	219
p-Diphenylylboronic acid	0·158	50% aq. C_2H_5OH	219

dilute organic solvents, and must be handled with care in an inert atmosphere. It is claimed as the most reactive boronic acid yet reported.[135] Vinyl boronic acids polymerize rapidly on exposure to air.[125]

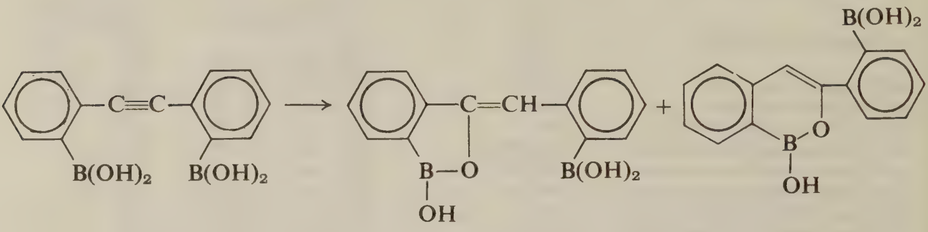
Boronic acids appear to have very weak directing effects in aromatic substitution.[14, 204, 209] The $B(OH)_2$ group is *meta*-directing in nitric acid solution and *ortho-para*-directing in acetic anhydride. Evidently the acetic anhydride carbonyl group co-ordinates with boron and reduces the aromatic–boron electron sharing.[14, 36, 208]



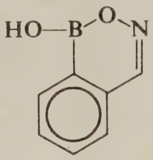


Nitration attempts with *m*-tolyl, 2-thienyl-, 2-naphthyl-, and *p*-methoxyphenylboronic acids resulted only in decomposition products which were evidently due to deborination reactions in the acidic solution.

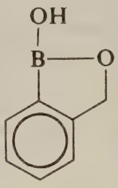
The $B(OH)_2$ group participates readily with reactive neighbouring groups[190]:



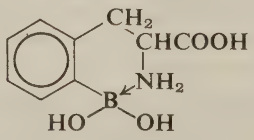
Neither the oxime nor the alcohol resulting from *o*-formylbenzeneboronic acid could be isolated. Instead the heterocyclic compounds resulting from neighbouring group dehydration were obtained[187, 191]:



and

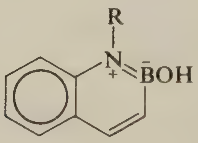


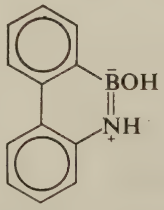
The borono–amino-acid *o*-boronophenylalanine does not show the characteristic zwitterion behaviour of most amino acids. This fact is attributed to co-ordination of the boron atom with the amino group of the amino-acid[164, 174]:



However, 2-aminopropylboronic acids appear to exhibit the normal zwitterion behaviour.[165] The aminoboronic acid, 2-dimethylaminomethylferroceneboronic acid, is soluble in both aqueous acids and bases and passes through an iso-electronic point.[134]

A series of heterocyclic boron–nitrogen compounds have been classed as 'hetero-aromatic' and much evidence has been put forward to show their aromatic properties (ultra-violet spectra, hydrolysis rates and stability to acids and bases)[192]:

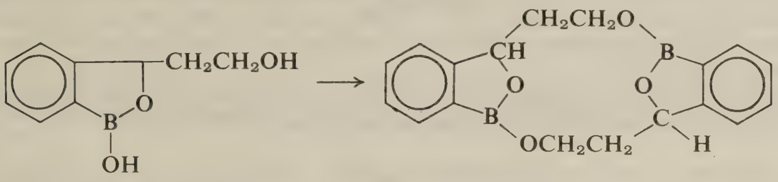




IV

In this respect, the borazaro–phenanthrene, **IV**, was found to be a proton acid and not a hydroxide acceptor.[133] This behaviour is unusual in boronic acids.

Boronophthalide shows chemical stability greater than that of most boronic acids in refluxing hydrochloric acid or potassium hydroxide. Deborination is also very slow with this compound. It may be nitrated in fuming nitric acid. Resistance to dehydration is shown by heating it at 80°C at 1 torr and by refluxing in thionyl chloride.[106] The hydroxyethyl derivative of boronophthalide shows the expected intramolecular co-ordination from oxygen to boron; it also forms an unusual dimeric anhydride *via* a bimolecular reaction[178]:



Methanetetraboronic esters are prepared by reaction of dimethoxyboron chloride, $(CH_3O)_2BCl$, with lithium and carbon tetrachloride in tetrahydrofuran. However, attempts to prepare the free boronic acid failed owing to deborination to methanediboronic acid. The difference in hydrolytic stability of the ester and the corresponding free acid was attributed to steric factors.[196] This interesting method for forming carbon–boron bonds appears significant for future synthesis.

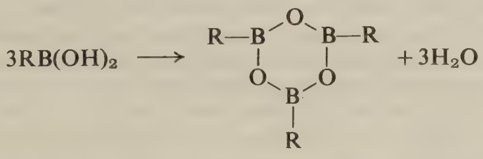
Particular Reactions of Boronic Acids

The following discussion of the reactions of boronic acids is divided into three parts: (1) reactions which involve the $B(OH)_2$ group itself under the heading 'Preparation of Boronic Acid Derivatives'; (2) reactions which remove the $B(OH)_2$ group from the original organic compound under the heading 'Deborination Reactions'; (3) reactions which have been carried out successfully in the presence of the $B(OH)_2$ group but do not involve this functional group directly under the heading 'Compatible Reactions'.

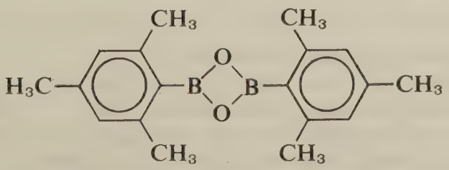
PREPARATION OF BORONIC ACID DERIVATIVES

Anhydrides

Boronic acids are easily converted to trimeric anhydrides by removal of water.



The resulting anhydrides are *B*-trisubstituted boroxines which have more reproducible melting points and are commonly used as derivatives for characterization of boronic acids. Formation of the anhydrides can be carried out by heating in a vacuum, by storage over phosphorus pentoxide or sulphuric acid, or by azeotropic removal of water using benzene, toluene or chloroform.[1, 106] A dimeric four-membered ring anhydride is formed from the sterically hindered mesitylene boronic acid[54, 243]:



Mixed boronic and carboxylic anhydrides are formed with appropriately substituted boronic acids.[155, 180, 205]

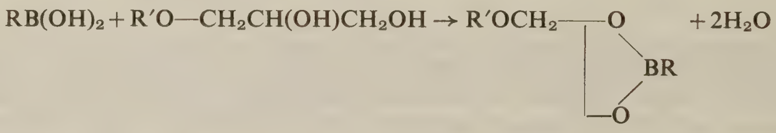
Esters

Another common derivative of the boronic acids is the ester formed from the reaction with a selected alcohol.

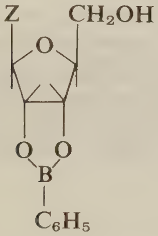
$$RB(OH)_2 + 2R'OH \rightarrow RB(OR')_2 + 2H_2O$$

The reaction is carried out by converting the boronic acid to the anhydride and then refluxing this with the alcohol.[106, 125, 127] Boronic acid esters are also formed by azeotropic removal of water with benzene and xylene[41] or by warming with alcohol on a steam bath.[48, 259]

Treatment of boronic acids with 1:2- and 1:3-diols gives the five- and six-membered dioxaborolanes and dioxaborinanes respectively.[66, 68, 87, 155, 185]



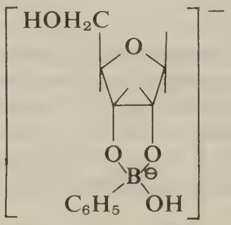
A procedure for purifying and characterizing boronic acids is to prepare the cyclic catechol di-ester.[155] Another application of the reaction with 1:2-diols is the formation of 2′:3′-esters of the *cis*-glycol groups on the sugar unit of the four common nucleosides:



Z = adenosine, uridine, guanosine, cytidine residues

Such a boronic ester has been used as a protecting group during phosphorylation, tosylation and tritylation. It can be prepared from the diol or the monophosphate and can easily be removed in water or with anhydrous propane-1:3-diol.[176]

Phenylboronic acid, like boric acid, complexes with sugars and other polyhydroxyl compounds. Acidity of the boronic acid is thereby increased and the complex may be titrated as a strong acid[96, 98, 208]:

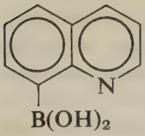


$H^{\oplus}$ $K_{eq} = 5{\cdot}2 \times 10^3$

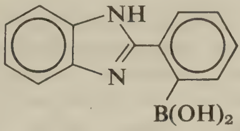
A review of this reaction has been published.[129]

Mixed esters with titanium[84] and with tin[93] have also been reported. Co-polymers of $C_6H_5NHCH_2SiCH_3(C_2H_5)_2$ and phenylboronic acid (1:1) show more hydrolytic stability than do poly-organoborosiloxanes which contain no amino groups.[50]

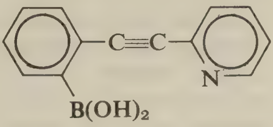
The amino-acid, 8-quinoline boronic acid (**I**), is an effective bifunctional catalyst for promoting the hydrolysis of 1:2- and 1:3-chlorohydrins to diols.[62–3, 71, 265] The same catalytic behaviour is exhibited by 2-(2-boronophenyl)benzimidazole (**II**), 2-(2-boronobenzyl)benzimidazole and, to a lesser degree, by 2-(2-pyridyl-2-ethynyl)-benzeneboronic acid (III).[76, 224, 266]



(I)



(II)



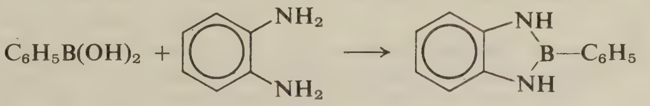
(III)

Both functional groups participate in performing the catalysis. The hydroxyl group first co-ordinates with the boron atom and the amino function then aids the chlorine removal.

Amide and Amine Complexes

Boronic acids form crystalline complexes with a variety of amines[129, 155, 212], e.g., ammonia, hydrazine, hydroxylamine, diethanolamine[9, 15, 40, 117, 245], pyridine[77, 221] and aliphatic amines.[221] A brucine complex was involved in the resolution of optically active 1-phenylethaneboronic acid.[107]

The reaction of boronic acids with orthophenylenediamine to give the *B*-nitrogen heterocyclic compounds, borabenzimidazolines, is often used to prepare crystalline derivatives[106, 155, 251, 259]:



Aliphatic 1:2-diamines do not undergo the corresponding reaction.[155]

Halides

A convenient method of preparation of boronic acids is usually the hydrolysis of the corresponding halogen derivative. However, the reverse reaction can be carried out by treating the boronic acid with boron trichloride, phosphorus pentachloride, or aluminium chloride.[59, 81, 129]

Salts

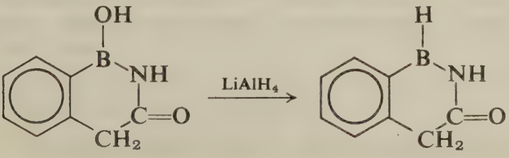
Salts of boronic acids are prepared by addition of the desired metal hydroxide to a concentrated aqueous solution of the boronic acid followed by precipitation with *iso*-propyl alcohol.[100, 238] In this manner lithium, sodium, potassium, calcium, barium and strontium salts have been isolated. Benzeneboronic acid is regenerated from its sodium salt by reaction with magnesium chloride[100]:

$$MgCl_2 + 2Na[C_6H_5B(OH)_2] \longrightarrow 2C_6H_5B(OH)_2 + Mg(OH)_2 + 2NaCl$$

The salts exist as Lewis-base adducts in which tetra-coordinated boron is involved. Little research has been done with salts of boronic or borinic acids and most of this has been published since 1964.[100]

Reduction Products

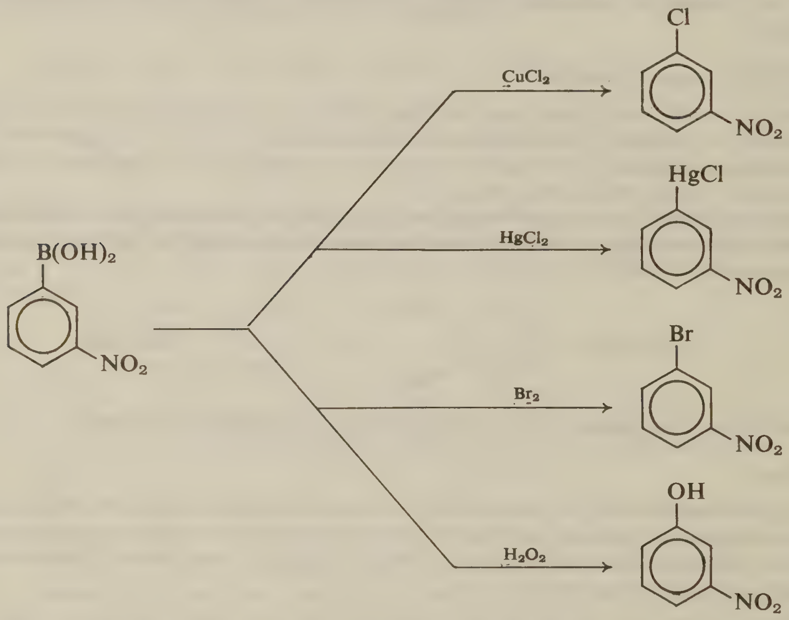
Reduction with lithium aluminium hydride gives the corresponding borane compounds[155, 179, 246–7]:



DEBORINATION REACTIONS

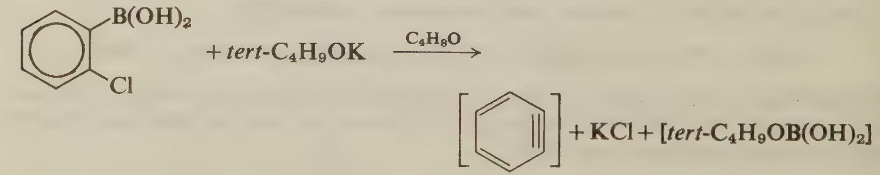
Reaction Conditions

Boronic acids undergo cleavage of the boronic acid function under a variety of conditions by reaction with acids, oxidizing agents (halogens, hydrogen peroxide, gaseous oxygen, chromic oxide and potassium permanganate), transition metal salts (mercury(II) chloride and bromide, silver nitrate, copper(II) chloride, cadmium bromide and zinc chloride), and bases (water, sodium hydroxide, ammonia and hydrazine).[13, 36–7, 48–9, 64, 80, 88, 119, 126, 203, 258–9] Reviews of this cleavage reaction have been given.[6, 129] The versatility of substituents obtained from deborination reactions recalls the well-known Sandmeyer reaction with amines[36]:



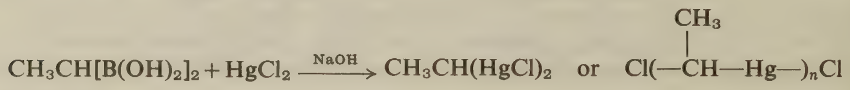
Alkyl boronic acids are more stable towards deborination than aromatic derivatives.[212] The more positive the substituent on boron, the more resistant is the acid to attack by electrophilic agents.[14]

o-Chlorobenzeneboronic acid is reported to form benzyne in the presence of a strong base[95]:



The same reactive intermediate forms during the aprotic diazotization of *o*-aminobenzeneboronic acid with *iso*-amylnitrite.[153]

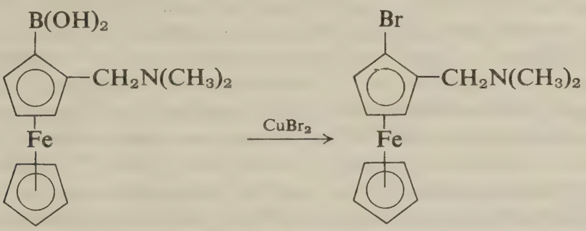
Electrolytic oxidation resulted in deborination of *n*-butylboronic acid, but benzeneboronic acid was ineffective.[184] Cleavage of ethane-1:1-diboronic acid with mercuric chloride gives ethylidenedimercuric chloride or an ethylene-mercury polymer[116, 147]:



$$CH_3CH[B(OH)_2]_2 + HgCl_2 \xrightarrow{NaOH} CH_3CH(HgCl)_2 \quad \text{or} \quad Cl(\text{—}\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{—}Hg\text{—})_nCl$$

The isomer, ethane-1:2-diboronic acid, when treated similarly gives ethylene, boric acid and mercurous chloride, but no organomercury compound.

The $B(OH)_2$ function in [2-(dimethylamino)methyl] ferrocene boronic acid was easily hydrolyzed to the hydroxyl or methoxyl group in aqueous and methanolic bases.[134] Stirring at 50°C with copper(I) chloride or bromide gave the halogenoamines[134, 171]:



An attempt to apply this type of reaction to tricarbonyl*cyclo*pentadienylmanganese boronic acid and the rhenium analogue failed to give the halogeno derivatives. Instead, copper salts were found to accelerate hydrolysis of the B–C bond in a hydrolytic deborination reaction.[226]

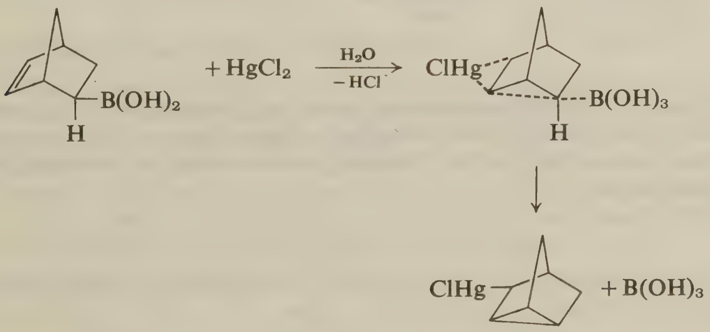
Ferrocenylboronic acid undergoes ordinary hydrolytic deborination when heated in hot water, but its aqueous recrystallization can be carried out rapidly.[177] The boronic acid derivatives of tricarbonyl*cyclo*pentadienylmanganese and rhenium are also readily hydrolyzed by water.[226]

Thiophene-2:5-diboronic acid hydrolyzes to thiophene and boric acid. It undergoes hydrogenolysis with Raney nickel to give tetramethylene diboric acid.[211]

Hydrolysis of alkene-1:1-diboronic acids also occurs easily[225]:

$$(CH_3)_2C{=}C[B(OH)_2]_2 \xrightarrow{\text{hot water}} (CH_3)_2C{=}CHB(OH)_2$$

Both *exo*- and *endo*-5-norbornene-2-boronic acids react with mercuric chloride to give nortricyclylmercuric chloride:



The *exo*-isomer which involves inversion of configuration reacts hundreds of times faster than the *endo*-isomer. This reaction is an example of transannular electrophilic displacement at a saturated carbon atom.[115, 188] The same reaction was studied in the *bicyclo*[2:2:2]oct-2-ene-5-boronic acid series.[189]

Photodeborination has been observed with ferrocene boronic acid and pyridine boronic acids.[199] Treatment of benzeneboronic acid with chlorosulphonic acid yielded only diphenyl sulphone.[203]

Mechanism of Deborinations

Oxidation of benzeneboronic acids with hydrogen peroxide has been investigated as an electrophilic displacement of the $B(OH)_2$ group.[2, 139]

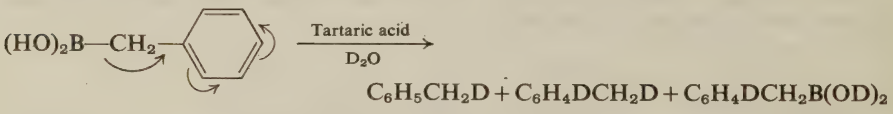
$$RB(OH)_2 + H_2O_2 \xrightarrow{NaOH} ROH + B(ONa)_3$$

This reaction is considered to be a good model for S_E2 reactions since no change of mechanism occurs when the group R is varied. The ions HOO^- and $H_3O_2^+$ are the oxidizing species, not molecular hydrogen peroxide. Oxidation with chromic acid is more sensitive to structure and sometimes gives rise to ketones.[55] Brominolysis of arylboronic acids gives a σ_p^+ correlation.[5]

A possible radical pathway is proposed when phenylboronic acid in pyridine solution is treated with ethyl α-acetylcinnamic ester $AcC(MCHPh)CO_2Et$ in the presence of a copper derivative of ethyl acetylacetate $AcCH_2CO_2Et$ to produce $AcCH(CHPh_2)CO_2Et$. In this case phenylboronic acid or triphenylborane(3) is used as the source of phenyl radical.[53] Deborination of alkylboronic acids, $RB(OH)_2$, with ammoniacal silver nitrate gave the hydrocarbon R–R, but the species RH is obtained with arylboronic acids.[1, 211] Evidence has been obtained for radical displacement of aryl and alkyl groups of boronic anhydrides.[203] The auto-oxidation of 1-phenylethylboronic acid shows a marked induction period in the presence of free-radical inhibitors such as galvinoxyl. This is taken as evidence of a free-radical chain process rather than the usually assumed polar cyclic mechanism. The free-radical nature of auto-oxidation of boron compounds has been reviewed[250] and the suggested mechanism is:

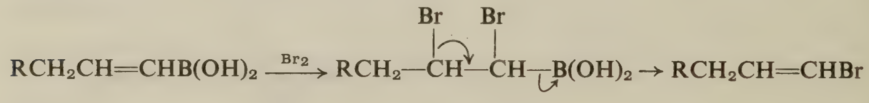
Initiation:	Production of R·, accomplished with free radical initiators
Propagation:	$R\cdot + O_2 \rightarrow RO_2\cdot$
	$RO_2\cdot + RB \rightarrow RO_2B + R\cdot$
Termination:	$R\cdot(RO_2\cdot) + R\cdot(RO_2\cdot) \longrightarrow$ non-radical products

Deborination of benzylboronic acid with tartaric acid in deuterium oxide was found to lead to incorporation of deuterium in the phenyl ring as well as at the benzyl position. This was attributed[240] to activation of the aromatic ring by hyperconjugation involving the boron–carbon bond:



$$C_6H_5CH_2D + C_6H_4DCH_2D + C_6H_4DCH_2B(OD)_2$$

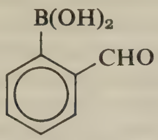
Optically active 1-phenylethaneboronic esters are deborinated with retention of configuration by trimethylamine oxide and octanoic acid and with net inversion by sodium deuteroxide.[170] Alkeneboronic acids undergo β-elimination reactions during bromination[106]:

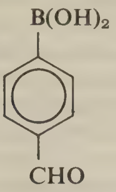


$$RCH_2CH{=}CHB(OH)_2 \xrightarrow{Br_2} RCH_2—\overset{Br}{CH}—\overset{Br}{CH}—B(OH)_2 \rightarrow RCH_2CH{=}CHBr$$

COMPATIBLE REACTIONS

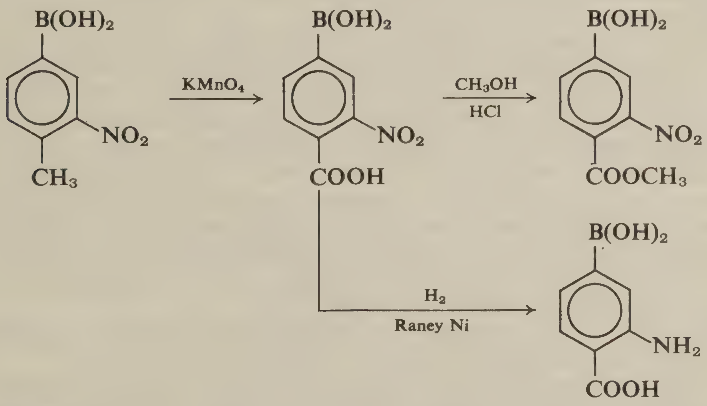
Such a variety of reagents cause deborination that it might be considered that the $B(OH)_2$ group is too labile for other reactions to be carried out in its presence. However, most of the reagents involved may also be used under mild conditions to effect a variety of reactions without disturbing the $B(OH)_2$ function. For instance, aromatic boronic acids have been halogenated successfully with chlorine or bromine in acetic acid and with dioxane dibromide complex. Iodine or iodine monochloride has also been used, but these reagents usually lead to electrophilic substitution of the boron portion.[66, 68, 77, 129, 204] Side-chain brominations with *N*-bromosuccinimide or bromine gave both the mono- and di-brominated products. This procedure, followed by hydrolysis of the bromine function, was used to prepare *o*- and *p*-formylboronic acids.[6, 146, 155, 173, 191, 202] The *o*-bromomethyl derivative was used to prepare the corresponding cyanomethyl compound by reaction on an ion-exchange column, Amberlite IRA 400, in the cyanide form[155, 180]:



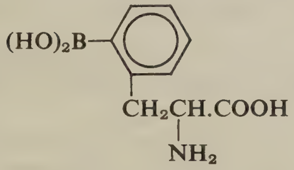


A procedure was developed for the chlorination of the methyl group of methaneboronic acid derivatives using *tert*-butyl hypochlorite and the pyridine complex of the boronic acid.[102]

Permanganate oxidations are carried out under mild conditions to avoid both ring opening and deborination.[191, 204, 220] This reagent was used to oxidize a boronosulphide in the preparation of 2-boronobenzyl methyl sulphoxide.[160] Fischer esterifications, hydrogen reductions, and acetylation of amines are also compatible[165, 204, 209]:



In addition carboxylic acids may be converted to the corresponding acid chlorides with phosphorus pentachloride and these may be reacted with amines or sodium azide to yield the boronic acid-amines or azides.[204, 209] Curtius rearrangements[204, 209], acid hydrolysis of amides[209], diazotizations[6, 14, 209], Michael condensations with nitromethane[191], and cyanohydrin formation[191] have been used successfully. A malonic ester condensation followed by acid hydrolysis and decarboxylation was used to prepare both the 2- and the 4-boronophenyl alanine[164, 174, 191]:



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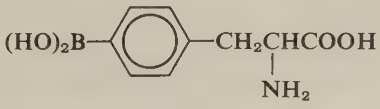
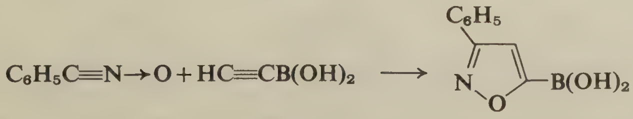


The addition of nitrile oxides to acetylene boronic acid gave isoxazoleboronic acids[159]:



The dibutyl ester of acetylene boronic acid was treated with ethyl diazoacetate and diphenyldiazomethane to obtain, after hydrolysis, heterocyclic pyrazole boronic acids.[38,138] Radical-induced additions to the double bonds of alkeneboronic acids have been carried out with bromine, hydrogen sulphide, and alkylthiols.[106,244] Polymers and co-polymers of vinylboronic acids are formed in the presence of free-radical initiators.[172] In some cases these unsaturated boronic acids are polymerized to give low-density 'pop-corn' type polymers. Iodine displacement from iodomethane boronic acid was accomplished with several nucleophilic reagents including alkoxides, amines, carbanions and mercaptides. This reaction when applied to mercaptopyrimidines resulted in a variety of boron substituted pyrimidines.[168]

Aromatic boronic acids undergo nitration in acetic anhydride[267], concentrated sulphuric acid[36,267] or fuming nitric acid[194], and the resulting nitroboronic acids may be catalytically reduced to give amino-boronic acids.[204,209,267] These may be diazotized and converted to phenolic boronic acids or to boron-containing azo dyes.[6,14]

Sulphonation was carried out in pure sulphuric acid to give the *meta*-substituted product, which was very hygroscopic, and was isolated as the sodium salt.[3]

Biological Effects of Boronic Acids

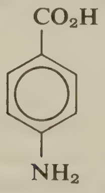
Aryl boronic acids were found to be slightly toxic to rats and mice; *o*-tolyl boronic acid was the most toxic of the group examined.[20] These materials are eliminated in the urine as boric acid and the parent aryl compound or its phenol analogue.[241] The LD_{50} for benzeneboronic acid fed to rats has been determined as 560 mg kg^{-1}.[203]

Aryl boronic acids have a root-growth-promoting effect on wheat, which involves cell elongation and not cell multiplication. In this, benzeneboronic acid was the best of 24 compounds tested followed by 4-methoxyphenylboronic acid. Both compounds increased the root growth by approximately 200% at the effective concentration range of 10^{-4} to 10^{-6} M.[13,21] The effect operates through the formation of complexes with polyols. Complexes of this type with sugar units of nucleosides are considered to be involved in the biological mechanism of boron as a required trace element. The 2′:3′-*o*-phenylboronate derivatives of the four biologically important nucleosides have been prepared and isolated.[176,182]

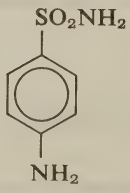
Benzeneboronic acid stimulates yeast formation by increasing the permeability of the cytoplasmic membrane. Boric acid is inactive in this respect.[144] This same boronic acid stimulates the activity of oxidative enzymes in peas and tomatoes and this stimulation results in a change of the morphology of the plants.[183] Abnormal flowers grew when this boronic acid was applied to the buds of plants.[234] In addition, benzeneboronic acid is a cholinesterase inhibitor[203,207], and *n*-alkylboronic acids reversibly inhibit the enzyme-catalyzed hydrolysis of amides and esters by α-chymotrypsin.[242] Cotyledon development of young undifferentiated *C. persicum* embryos was inhibited by 2×10^{-3} M phenylboronic acid solution.[256]

Benzene- and *p*-tolueneboronic acids are condensed with 1:2- and 1:3-diols to give dioxaborolanes and dioxaborinanes which are useful as analgesic and tranquillizing agents.[45,68] Benzeneboronic acid has synergistic effects by increasing the normal activity of several hypnotics.[214]

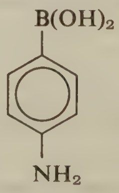
As a result of the relationship to *p*-aminobenzoic acid, **V**, and sulphonilamide, **VI**, a series of substituted aromatic boronic acids was tested for activity against micro-organisms. *o*-Hydroxymethylbenzeneboronic acid was found to be only slightly less active than sulphathiazole and sulphadiazine. *p*-Aminobenzeneboronic acid, **VII**, was unstable in air and showed even less activity than benzeneboronic



V



VI



VII

acid.[207] Benzeneboronic acid and the *o*-, *m*-, and *p*-nitro derivatives showed moderate bacteriostatic activity against *staphylococcus aureus* in an order of activity: nitrophenylboronic acids > benzeneboronic acid > boric acid. The corresponding hydroxybenzeneboronic acids were inactive even though phenol and cresol are active.[209]

Boronic acids and their derivatives have shown activity as chemosterilants for house-flies. This activity was enhanced with some esters and amides which release the boronic acid in aqueous systems.[227] Benzeneboronic and *m*-chlorobenzeneboronic acid have insecticidal properties. The *m*-chloro derivative was reported to be as effective as DDT on the four species tested.[216]

In the cancer therapy programme several boronic acids were found to have a favourable tumour-to-brain ratio.[152, 235]

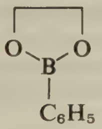
Uses of Boronic Acids

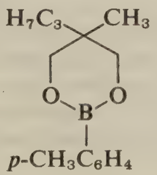
Some alkaneboronic acids have been offered commercially, and benzeneboronic acid was once available[228], but no large-scale use of these materials has developed.[136] Hydrolytic instability and the high cost of manufacturing processes involving Grignard reactions are the main reasons for lack of commercial development.

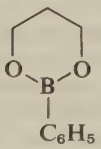
Alkaneboronic acids were used as oxidation inhibitors in oils[27, 123, 233] and in gasoline or petroleum spirit; they also retard the formation of residues in gasoline.[232] By far the largest application of boronic acids has been for incorporation into various polymers with the aim of modifying the polymer characteristics. A polymeric film prepared by heating phenylboronic acid and diphenyldihydroxysilane was applied to copper plate to give an electrically insulating film.[7] Clear, transparent films were prepared from the polymer formed by heating benzeneboronic acid with 1:6-hexylenedi-isocyanate.[8]

Benzenediboronic acids[51] with long-chain dihydroxylic alcohols form polymers which are reported to produce films and fibres.[17, 33, 51] Polyesters of boric acid and alkaneboronic acids prepared as elastomers for neutron shielding were shown to have poor hydrolytic and oxidative stability.[42] Polymers obtained by first reacting *p*-phenylene or polymethylenediboronic acids with trihydroxy compounds followed by condensation with di-isocyanates or di-isothiocyanates are said to possess good adhesive properties as well as excellent hydrolytic stability. Mouldable and extrudable polymers with good metal-to-metal binding properties are obtained by modifying polyethylene and polypropylene with *p*-vinylphenylboronic acid, *p*-$CH_2{=}CH\text{-}C_6H_4B(OH)_2$.[113] The dye receptivity of polyvinyl alcohol increases on esterification with butaneboronic acid.[230] Polymers stable thermally to 500°C are claimed from the condensation of benzenediboronic acid with organotin and organozinc compounds.[231]

Boronic and borinic acids and anhydrides of boronic acids are effective as vinyl-polymerization catalysts for polar monomers[60, 128] and as stabilizers for polyolefins.[229] Alkane and areneboronic acids and anhydrides are used as stabilizers for hydrocarbon polymers to improve their oxidation, heat and light resistance.[118] Benzene and *p*-tolueneboronic acids are condensed with 1:2- and 1:3-diols to give dioxaborolanes and dioxaborinanes which are useful as antioxidants in polymers[112]:





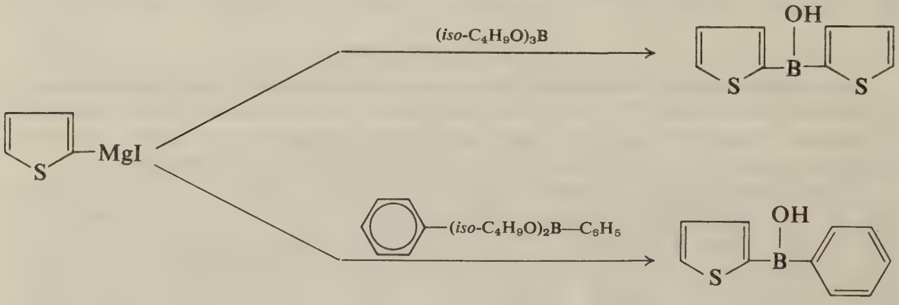


A recent use of boronic acids has been to convert high-boiling or unstable materials into cyclic derivatives which can be successfully separated by gas chromatography. Suitable derivatives are easily formed with 1:2-diols, 1:3-diols, 1:2-enediols, and α-hydroxyamines. *n*-Butylboronic acid is favoured in this application. Derivatives are formed at room temperature in less than 15 min reaction time. The boronic acid derivatives of steroids, fatty acids and glyceryl ethers have been successfully examined gas-chromatographically.[263–4]

BORINIC ACIDS

Preparation of Borinic Acids

As with boronic acids the commonest method of preparation of borinic acids is *via* the Grignard reaction; in this case, however, a ratio of two moles of Grignard reagent to one of boron compound is required.[4, 9, 29, 46, 89, 270] Bis(2-thienyl)borinic acid and phenyl-2-thienyl-borinic acid were prepared in this manner[78]:

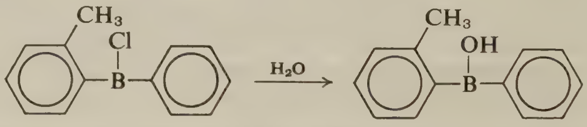


A very small yield of diferrocenylborinic acid was isolated by column chromatography as one of the products from the reaction of lithioferrocene with boron trifluoride etherate.[239] Preparations similar to those discussed for boronic acids involving hydrolysis or oxidation require the dialkyl- or diarylboron derivatives. An example involving both the Grignard and hydrolysis reactions is[9, 58]:

$$2CH_2{=}CHCH_2MgBr + BF_3 \xrightarrow[-10°C]{H_2O,\ NH_4Cl} (CH_2{=}CHCH_2)_2BOH \xrightarrow{-H_2O} [(CH_2{=}CHCH_2)_2B]_2O$$

Since borinic acids are usually liquids, purification is often effected by distillation which can result in formation of the anhydride. A more successful isolation and purification method involves formation of the amino-ethanol chelated ester discussed on p. 804. Purification procedures involving conversion to the ethyleneglycol ester have also been discussed.[9]

Unsymmetrical borinic acids are obtained by hydrolysis of the corresponding chloro-derivative.[16] Disproportionation of these compounds would be expected to be especially facile:



Diphenylborinic acid may be isolated as a mixed anhydride by reaction of sodium tetraphenylborate with an amino acid.[257] Similarly, reaction of sodium tetraphenylborate with 8-hydroxyquinoline, 2-aminoethanol, and pyridine-2-carbinol yields diphenylborinic acid complexes.[130, 131] Preparation of diphenylborinic acid from sodium tetraphenylborate is not as convenient and reliable as the Grignard method with ethanolamine isolation.[72]

Dimethylborinic acid was prepared in 75% yield by heating trimethylborane with water at 200–220°C. The *o*-deutero derivative was prepared in the same manner using deuterium oxide[249]:

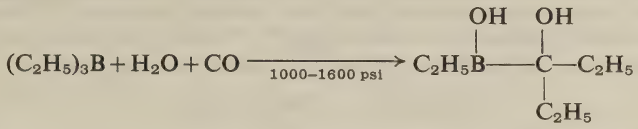
$$(CH_3)_3B \xrightarrow[200-220°C]{H_2O} (CH_3)_2BOH + CH_4$$

However, at 310°C the boronic acid system is predominant[249]:

$$(CH_3)_3B \xrightarrow[312°C]{H_2O} \underset{90\%}{(CH_3BO)_3} + \underset{5\%}{CH_3B(OH)_2} + \underset{5\%}{[(CH_3)_2B]_2O}$$

Trialkyl boranes may also be oxidized to borinic acids using a 1:1 ratio of amine oxides.[186]

An unusual preparation has been recorded in which triethylborane was treated with carbon monoxide and water at 1000–1660 lb in^{-2} to give ethyl(3-hydroxy-3-pentyl)borinic acid[167]:



$$(C_2H_5)_3B + H_2O + CO \xrightarrow[1000\text{–}1600\ \text{psi}]{} C_2H_5\overset{OH}{\overset{|}{B}}\text{——}\underset{\underset{C_2H_5}{|}}{\overset{OH}{\overset{|}{C}}}\text{—}C_2H_5$$

Similar reactions were carried out with tri-*iso*butylborane, tri-*n*-hexylborane and tri*cyclo*hexylborane.[167]

Physical Properties of Borinic Acids

Many borinic acids are liquids or waxy solids[9, 86, 145]; however, several crystalline aromatic analogues are known.[4] Boiling points reported for liquid borinic acids and melting points for solids quoted in Tables I and II are probably those of the anhydrides in many cases.

Vapour-pressure measurements of dimethylborinic acid in *n*-butane solution indicate a complex molecular association greater than the simple dimeric or trimeric system.[175] The following variation of the vapour pressure with temperature has been observed.[249]

Table VIII.—Vapour Pressure data for Dimethylborinic Acid

Temperature (°C)	0·4	4·6	10·5	14·5	18·0	22·0	25·3	28·6	35·0	40·9
torr	36	49	70	91	110	140	168	201	281	377

The gas phase i.r. spectrum of dimethylborinic acid has the hydroxyl stretching frequency at 3675 cm^{-1} which resolves to a triplet at 3682, 3672 and 3662 cm^{-1} in a high-resolution instrument; the triplet is attributed to the monomer. A 5–10% solution in carbon tetrachloride gave a characteristic hydrogen-bonding pattern with two absorptions of 3635 cm^{-1} (half-width 27 cm^{-1}) and 3375 cm^{-1} (half-width *ca.* 250 cm^{-1}). The latter—a smooth curve with no fine structure—was assigned to the hydrogen-bonded species.[175] For diferrocenylborinic acid the hydroxy-absorption band appears at 3590 cm^{-1} in a nujol null.[239]

The hydroxyl proton in the n.m.r. spectrum of dimethylborinic acid varies considerably with temperature and concentration. This behaviour and the broad absorption in carbon tetrachloride are characteristic for hydrogen-bonded protons. At 36°C for the neat liquid, hydroxyl and methyl peaks appear at 1·28 τ and 9·64 τ respectively.[175] The n.m.r. spectrum of diferrocenylborinic acid shows the proton of the BOH groups at 1·4 τ. The mass spectrum of diferrocenylborinic acid is also reported.[239]

Thermochemical methods were utilized to obtain the standard heat of formation of crystalline $[(C_6H_5)_2B]_2O$ as diphenylborinic acid anhydride ($-84{\cdot}0 \pm 2{\cdot}0$ kcal mole^{-1}).[145] The value for the free acid, $(C_6H_5)_2BOH$, was determined using data from the hydrolysis of liquid diphenylboron chloride to be $-77{\cdot}4 \pm 1{\cdot}8$ kcal mole^{-1}.[141, 145] The standard heat of formation of dibutylborinic anhydride is given as $-212{\cdot}8 \pm 1{\cdot}3$ kcal mole^{-1}, and its standard heat of combustion is $-2{,}839{\cdot}7 \pm 1{\cdot}1$ kcal mole^{-1} [108] for the reaction[109]:

$$[(C_4H_9)_2B]_2O + 26O_2(g) \longrightarrow 2H_3BO_3(\text{cryst.}) + 15H_2O(l) + 16CO_2(g)$$

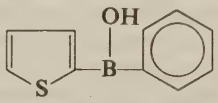
Chemical Properties of Borinic Acids

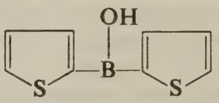
Borinic acids as a group are less stable than the boronic acids to air oxidation and disproportionation. On storage, a borinic acid tends to form the corresponding boronic acid and the hydrocarbon.[4, 72, 212] For stability on storage they are usually converted to the ethanolamine ester and then liberated as needed.[72] During distillation they are readily converted to anhydrides[86, 212] or they disproportionate to form trialkylboranes and anhydrides of the corresponding boronic acids[9]:

$$3(R_2B)_2O \rightarrow (RBO)_3 + 3R_3B$$

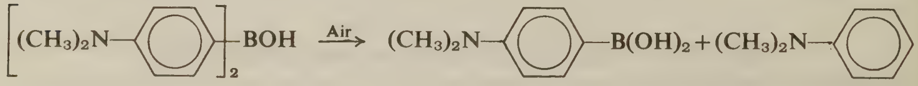
Borinic acids may be oxidized completely to boric acid in air or with hydrogen peroxide or the halogens.[212]

Phenyl(2-thienyl)borinic acid and bis(2-thienyl)borinic acid are unstable in air and are isolated as the oxidates of 8-hydroxyquinoline. As free acids they tend to disproportionate giving benzene and thiophene, respectively, and the corresponding boronic acid[78]:

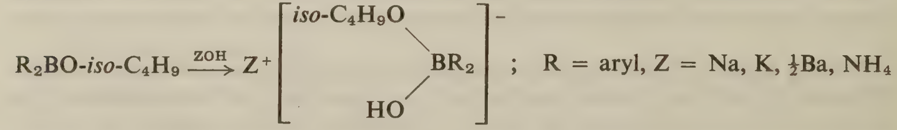




Bis-*p*-dimethylaminophenylborinic acid could only be isolated as its 2-aminoethanol derivative.[229]



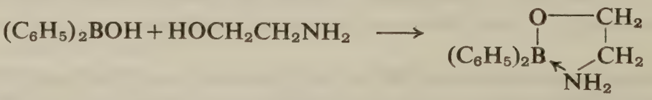
Diaryl borinic esters may be converted to salts in basic solution. These salts undergo hydrolysis in acid solution to give the borinic acids.[4]



$$R_2BO\text{-}iso\text{-}C_4H_9 \xrightarrow{ZOH} Z^+\left[\begin{matrix} iso\text{-}C_4H_9O & \\ & BR_2 \\ HO & \end{matrix}\right]^- ; \quad R = \text{aryl}, Z = \text{Na, K, } \tfrac{1}{2}\text{Ba, NH}_4$$

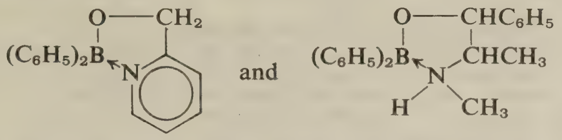
Reactions of Borinic Acids

Procedures for the preparation of anhydrides and esters of borinic acids resemble those used for boronic acids.[4, 9, 58, 79, 86, 212] The major difference is the much greater problem of disproportionation with borinic acids. Therefore, considerable effort has been exerted in preparing stable derivatives from which the parent compounds can be liberated when required. The commonest procedure involves conversion to the corresponding aminoethylborinate by reaction of the borinic acid with 2-aminoethanol:

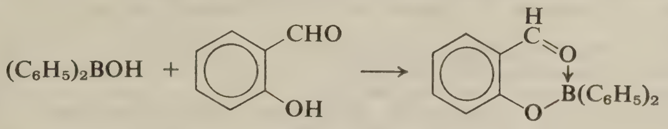


$$(C_6H_5)_2BOH + HOCH_2CH_2NH_2 \longrightarrow \begin{matrix} & O & \text{---} & CH_2 \\ (C_6H_5)_2B & \leftarrow & NH_2 & CH_2 \end{matrix}$$

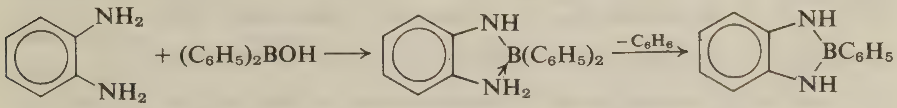
These chelated derivatives are stable towards hydrolysis and air oxidation and can be stored for long periods. The free acids can be liberated when needed by hydrolysis in aqueous acid.[9, 72, 86, 101, 161–2] Other amino-alcohol chelated ester derivatives have been prepared from 2-pyridylalkanols[79], ephedrine bases[44, 129] and 8-hydroxyquinolines[185], e.g.,



Other stable chelates are formed from β-ketoesters[70], nitrosophenylhydroxylamine, salicylaldehydes and the corresponding azomethines, e.g.[185],



If one of the chelate groups has a labile proton, benzene may be split off and the corresponding heterocyclic ring is formed[185]:



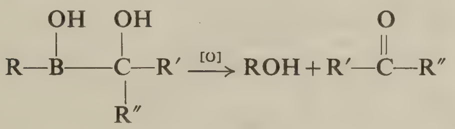
With heterocyclic nitrogen bases diphenylborinic acid forms co-ordination compounds which may be used as solid derivatives.[223]

Uses of Borinic Acids

Dialkylborinic acids have been reported along with alkylboronic acids as anti-knock additives in gasoline when mixed with familiar lead materials.[23] These same materials plus diphenylborinic acids are also used as ice-preventing agents in jet fuels[28], and as antioxidants in rubber to retard cracking and discoloration due to ozone.[97]

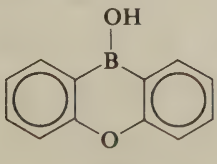
Esters of epoxy alcohols with borinic acids are patented for use as stabilizers in vinyl chloride polymers and for making epoxy resins.[105] Similar esters with polyvinyl alcohol using dibutylborinic and diphenylborinic acids were used to modify the solubility and melting characteristics of the parent polymer.

An unusual preparation of ketones and alcohols results from the high-pressure carbonylation of trialkylboranes which gives hydroxyborinic acids. These are then oxidized to give the desired ketones or alcohols which are otherwise difficult to make[167]:

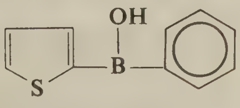


$$R{-}\overset{\displaystyle OH}{\overset{|}{B}}{-}\underset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}R' \xrightarrow{[O]} ROH + R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R''$$

Diarylborinic acids were used as analytical reagents in detecting microgram quantities of 3-hydroxyflavones and hydroxyphenyl-benzo-8-pyrone coupled with u.v. spectroscopy.[213, 215] Both 10-boroxanthydrol, **VIII**, and phenyl-2-thienylborinic acid, **IX**, are specific reagents used in determining the stereochemistry of ephedrine and pseudoephedrine.[103]



VIII



IX

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